

Researches
on the
Affinities of the Elements

GEOFFREY MARTIN

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16/11/2014

Researches
on the
Affinities of the Elements
and on the
Causes of the Chemical Similarity or
Dissimilarity of Elements and Compounds

By **Geoffrey Martin**, B. Sc. (Lond.)

With five woodcuts, one large plate, fourteen tables and three appendices

London
J. & A. Churchill
7 Great Marlborough Street
1905

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Preface.

The following pages contain the first attempt which has been made to systematically collect together data regarding the varying in stability of the different compounds which an element produces with other elements, with the object of discovering the law regulating the chemical attraction the elements mutually exert on each other.

I think the following researches completely solve this problem, the affinities of the successive elements following what is referred to below as the "wave law" which is described in chapter V, and exhibited graphically on the large plate at the end of the book.

This result is quite new; in fact, it only became possible to discover it because of the elaborate investigations which have been carried on within the last few years on the nitrides, carbides, silicides, borides &c. of the elements. Only ten years ago the data required to demonstrate the law was entirely wanting — a fact, which affords a striking example of the rate at which inorganic chemistry is developing.

The work of collecting and arranging the data was extremely laborious, as most of the facts had to be obtained out of the current periodicals. Each of the 31 affinity surfaces described in chap IV required usually about three weeks hard work to produce. It was only after months of what seemed to be fruitless labour that I suddenly became conscious that a definite law underlay the mass of data I had collected, and that the elements did actually attract each other according to a distinct rule.

The best way to make this law apparent is to read through chapters IV and V and then look at the pictures of the affinity surfaces given in the large plate at the end of the book.

It will then be seen that the affinity surfaces of the successive elements take the appearance of successive positions of an advancing wave, which repeats itself at the end of every fresh cycle of elements of the Periodic System.

A study of these affinity surfaces of the elements will convince the reader that the current custom of chemists of regarding some elements as possessed of only feeble affinities, and others as possessed of strong affinities is to a great extent erroneous.

Nearly every element (except some of the very heavy ones) is shown by these researches to possess very strong affinities for certain elements, and very weak affinities for other elements; take, for example, the case of nitrogen; at the present time, I think, everybody looks upon nitrogen as an element characterised by the feebleness of its affinities. In chapter IV and V, however, we show that this is entirely incorrect; nitrogen is shown to possess very powerful affinities for certain elements, and very feeble affinities for others, just in the same

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way that oxygen or sulphur possess very strong affinities for some elements and feeble ones for others — the only difference being that nitrogen exerts its greatest attraction on elements which are different from those which O or Cl exert them on; for example, the nitride NP is so stable that it must be heated in oxygen gas to above the temperature whereat hard glass melts before the oxygen begins to attack it!

Again, carbon and silicon are commonly referred to as being remarkable and abnormal as regards their power of self combination. A glance at the affinity surfaces exhibited on the large plate at the end of the book will show that this power of self-combination is to be expected on account of the wave law of affinity above referred to, the carbon and silicon exerting their greatest chemical attraction not on other atoms (as do O and Cl) but on their own atoms. The law followed in both cases is the same. As a result of this "Wave Law" the old notion that only chemically unlike elements combine strongly together, and that all chemically similar elements combine feebly together, must be abandoned. For example, carbon exerts a very great chemical attraction on silicon, and a still greater attraction on its own atoms.

A brief abstract of the wave law was published in the *Chemical News* (1904). 90. 175, but the full statement and data on which it rests appears in print in the following pages for the first time.

It will possibly appear to my readers that it would have been better to arrange the affinity data graphically in the form of curves, and not as surfaces as I have done. The suggestion arises partly on account of a lack of practical experience of the subject, and partly on account of the fact that when they are once used to dealing with surfaces, they will find, that they exhibit far more clearly and concisely than curves can do, the relationship that the affinities a given element possesses for an atomic species bears to those which neighbouring elements possess for the same atomic species. The rise or fall in the slope of the affinity surface as we pass transversely across it, indicates precisely the rise or fall of affinity for this atomic species as we pass from one distinct group of elements of the Periodic System to another. While the rise or fall of the slope of the surface as we pass longitudinally down it indicates the rise or fall of affinity as we pass from one element to another of the same group of the Periodic System. The relative fluctuations in the affinities of neighbouring elements for a given atomic species are thus indicated with a distinctness and conciseness such as could never be attained by the alternate method of using a long sinuous curve. In the early part of my researches I actually used curves instead of surfaces, but abandoned their use after the advantages of the latter method became apparent through trial.

Another point which may be criticised, and perhaps with justice, is the fact that I have constructed the affinity surfaces of the elements with respect to about only half the known elements.

My critics will perhaps pardon me when they properly understand the enormous labour which is required to construct an affinity surface relating to all the elements. For a single element forms many hundreds of compounds with all the other known elements, each of which must have its reactions and stability

minutely studied before we can arrive at a notion of the attraction the element possesses for other elementary atoms -- a study which requires weeks, nay, sometimes months of work, since much of the data must be extracted out of the papers of the original investigators. The construction of such complete affinity surfaces is a task beyond the time at my disposal, especially as in the case of many elements the data is so defective as to make the task almost hopeless. I have carried the researches far enough to make clear what law does regulate the affinities the elements mutually exert on each other, and any extension of this research would probably only confirm the conclusions previously arrived at. As it is, the task has taken me nearly a year and a half of most laborious work on this section of the book alone.

It is asserted as a fundamental proposition that the chemical and physical properties of an element depend almost entirely upon the attractional forces it exerts upon the atoms of other elements.

From the very nature of the proposition it is hard to give a direct proof of this, though one is attempted in chap. I pp. 10--17.

My own conviction of the truth of the proposition was gradually formed as the result of a minute study of the different reactions which different elements and compounds undergo (a few of which are set forth in chap. II) which are impossible to reproduce here without at the same time writing a formal treatise on descriptive chemistry. The reader will probably only share my own conviction in this respect after he has subjected himself to the same process that I did -- namely, to systematically set to work to contrast minutely the analogous reactions of chemically similar elements, and to continually ask himself as his studies proceed, the question "Why do there exist these slight but perceptible differences in the way these chemically similar atoms react?"

The answer will always be "because of the slightly different chemical forces they exert on the same atoms". He will invariably find that the more widely do their reactions differ, the more widely do the forces they exert differ. From this standpoint to the complete generalisation is but a step which will be forced upon him when he begins to contrast chemically unlike elements. The result is in itself exceedingly probable when we remember how enormously more mighty are the chemical forces than any others which the atoms exert. The gravitational forces they exert fade into absolute insignificance compared with them.

For example, judged from their heat of combination, the chemical forces which H and O atoms exert on each other are 71 billion times greater than the gravitational forces they exert! *)

Indeed it is shown in chapter II that it is probably these chemical forces alone, at play within the molecule, which determine almost completely the forces the molecules themselves exert on each other, and so their fusibility, volatility, solubility and cohesion.

Our proposition, in fact, simply amounts to the statement that the chemical forces which the atoms of an element exert are so much more mighty than any

*) Helmholtz. Jr. Chem. Soc (1881) 39. 277.

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other forces they exert that they determine almost entirely the properties of the element, namely, its chemical reactions, its volatility, fusibility, solubility, cohesion &c. &c. Many physicists share this view, only instead of chemical forces they use the term "electric forces". If the reader still doubts the truth of this proposition after studying the data set forth in the following pages, I would beg him to consider what alternate factors other than the chemical forces are there which could determine the properties of an element? Certainly the gravitational forces which the atoms of the elements are capable of exerting on each other, are far too small to be of any appreciable influence. There are, in fact, no known factors other than the chemical forces they exert which are powerful enough to govern completely the motions of the atoms, and thus to decide their behaviour. Another important result established in the following pages (chap. II) is the fact that chemically similar elements attract the same radicles or atoms with proportional intensities of force, and that the more nearly equal are these forces, the more alike chemically are the elements.

As to the correctness of this result, there can, I think, be absolutely no doubt. My experience extends over too wide a range of facts — embracing almost every element in Inorganic Chemistry — to admit of a mistake. Not a tythe of the evidence on which my conclusion is founded is set forth in chapter II. There is only given there what is regarded as sufficient to demonstrate the law. An examination of the thermal data (which incidentally proves the substantial correctness of Berthelot's and Thomsen's conclusions — namely, that the heat of combination of a compound does measure very roughly the attractive force driving together the atoms in the molecule) set forth in chapter II, and the reactions of the elements given in section 3 of the same chapter, as well as the fact (chap. V p 181) that chemically similar elements possess geometrically similar affinity surfaces, can leave no doubt as to its correctness.

I should like to say a few words as to the theoretical importance of the law just mentioned. The general fact has long been known that there exist groups of elements all of which betray the greatest chemical similarity to each other; and that other elements exist which do not exhibit the smallest chemical resemblance. Why is this? Why, for example, does chlorine resemble bromine in its chemical behaviour, and why does it differ widely from (say) oxygen or nitrogen? Why is sodium so similar to potassium and so different from carbon? These are the questions which one would have expected would have been the very first to engage the attention of chemists. But this has not been the case. Not one of the published textbooks in chemistry, nor, so far as I am aware, a single chemical author, utters a word upon this question, or even seems to be aware that there is anything to explain!

Indeed the researches contained in chap. II are the first investigations that have ever been undertaken to decide the factors which determine the chemical similarity or otherwise of the different elements, and this although chemistry as a science has been in existence nearly 150 years! The law above established gives the complete answer to the questions.

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Such investigations take us down to the very foundations of Inorganic Chemistry, and moreover are of prime importance because they give us the possibility of explaining that remarkable recurrent graduation of properties of the elements which is comprised under the name of the "Periodic Law".

For the periodic law shows that as the atomic weight increases the properties of the successive elements gradually alter and then at the end of a cycle suddenly return to nearly but not quite their original values.

And our researches lead to the conclusion that the properties of the elements depend solely upon the forces they exert on other atomic species, and that chemically similar elements exert proportional attractive forces.

Therefore, to give a mechanical explanation of the Periodic Law, we have only to find an explanation of the fact that as the atomic weights of the elements increase, the affinities they exert on other atomic species gradually alter, and then suddenly return at the end of a cycle to values proportional to those they originally had.

In this connection I have long been considering whether it would not be possible to look upon each of the different sorts of atoms as being simply a centre of strain in a universal granular medium; the strains being caused by an irregular arrangement of the particles composing the medium (something after the manner of Prof. Osborne Reynold's theory of the Universe). The number of possible ways of setting up strains of different intensities by altering the relative position of the particles of the medium, would then be the number of different atomic species.

If now we could only contrive to arrange the construction of these centres of disturbance in the symmetrical structure of the medium such that they tended to be impelled towards the other centres of disturbance in the medium according to the law of affinity (the Wave Law) shown in chapter V to govern the mutual attraction of the atoms for each other, we would have a complete mechanical theory of the elements, their properties, and the Periodic Law.

The researches which follow, show that it is undoubtedly possible to invent such a theory and I have already made some progress in this direction, the results of which I hope to publish separately.

I wish especially to call attention to some particular investigations given in chapter II, on the cause of the analogy between fluorine and oxygen (pp. 69 to 78), the causes of the chemical similarity of boron and silicon (pp. 79—84), of water to hydrofluoric acid (pp. 85—88), &c., &c., all of which bring quite new facts to light. Also the results brought to light by a comparative study of the volatility of different compounds are new — viz, that unstable compounds are as a whole more volatile than stable compounds, and that high grade compounds are more volatile than low grade compounds. An important use of this fact is made in chapter III on the theory of solution, in order to explain how it is that all cases of solution reduce to the case where the molecules of the liquid attract each other more strongly than they attract the dissolved molecules.

Many of the results of chapter II appear here in print for the first time; part, however, has already been published in abstract form. For example, the

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article entitled "The causes of the analogy between fluorine and oxygen" pp. 69 to 78 appeared originally in the *Chemical News* (1904). 89. 49. The results of pp. 107—123 on the volatility, solubility, &c. of the various compounds were briefly summarised in an article entitled "The connection between the volatility of compounds and the chemical forces at play within the molecule" which appeared in the *Chem. News.* (1904). 89. 241. The article (pp. 79—84) "The causes of the chemical similarity of boron and silicon" and "The chemical analogy of water and hydrofluoric acid" (pp. 85—88) bring new facts to light and here appear in print for the first time. The results of pages 41—55 will appear shortly in the *Journal of Physical Chemistry*.

It is a widespread notion that the molecular weight exerts a predominating effect in determining the melting and boiling points of compounds. The data brought together in Chapter II shows, I think, that this idea is to a great extent erroneous. The molecular weight is shown to exert quite an inappreciable influence as compared with that of the chemical forces in deciding the volatility, fusibility and solubility of compounds. The influence of the molecular weight is shown to become appreciable only when we contrast chemically analogous compounds — that is, compounds in which the attractive forces at play within the molecules are of the same order of magnitude; or else gasified compounds whose molecules are so widely separated that the influence of the chemical forces becomes inappreciable.

Helmholtz has shown*) how enormously more mighty are the chemical forces which hold the atoms together in the molecule than the gravitational forces which the atoms exert.

It is therefore not surprising that the influence of the molecular weight almost entirely disappears so long as the molecules lie so close together (as in the liquid and solid state) that the chemical forces exert an appreciable external influence. In cases, however, where the molecules are analogous, or where they lie far apart (as in the gaseous condition) the magnitude of the molecular weight then plays a predominating rôle.

After the cause of the chemical similarity or otherwise of different substances became clear, it was natural to consider what light this threw on the fact that chemically similar substances are miscible in all proportions, and chemically unlike substances usually immiscible. Chap. III grew out of this inquiry and gives a quite simple explanation not only of this fact, but also of many other facts of importance in the theory of solution, such as, for example, van't Hoff's Law of osmotic pressure, why there exists, in general, a limit to the solubility of different bodies in each other; why the solubility increases with the temperature &c., &c. This part of the work has already appeared in print in the "*Journal of Physical Chemistry*", Febr. 1905 — Vol. 9 p. 145 under the heading "A contribution to the theory of solution".

The treatment is novel and I wish especially to call physical chemists attention to this section of the work, since it opens up a new field of research.

*) See page V.

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Chapter I of the book is theoretical, and may be omitted, if the reader prefers, without much affecting what comes after. The chapter should be read in connection with chap. VI, which is really a continuation of it. In these chapters we start from the fundamental proposition that the properties of an element depend almost entirely upon the forces with which it attracts other elementary kinds of atoms; so that by representing these forces graphically we represent graphically the properties of the element. We then show that in consequence of this fact it is possible to reduce chemistry to a branch of applied mathematics, the magnitudes of the affinities an element exerts, being taken as the coordinates which determine its properties, in the same way that the magnitudes of the coordinates of a point in space determine its position.

In consequence of this circumstance, all changes in the properties of an element or compound can be expressed by an analytical expression (chapter VI) which is the expression of the changes in the values of the coordinates (ie. the affinities) which determine the properties of the element.

I also succeed in chapter I (pp. 23—32) in showing how to deduce the equation of the affinity surface. The general methods there applied can, of course, be altered to suit any similar problem.

It may be asserted that the methods advocated in chapter I and VI can have no practical value on account of the complexity of the resulting formulae. This may or may not be so, though the matter is open to doubt, seeing that our knowledge of the different grades of compounds producible by an element are in the highest degree defective. We are only acquainted with a few of the stablest compounds an element produces. The unknown, because unstable, compounds are infinitely more numerous than the known. When we begin to have a knowledge of the valency compounds of all grades which an element can produce, it will be then, and not before, that we can decide whether the method is a practical one or not. Again, it is of no concern whatever to a scientist, whether or not the phenomenon he investigates has a practical value or not. He is primarily concerned with the investigation of Nature, quite indifferent as to whether his investigations have a practical value to the chemical manufacturer or not.

Again, it may be said that the methods are not rigid, but give a definiteness to the phenomena which does not in reality exist. This I entirely deny. If the properties do depend upon the affinities, the treatment is mathematically rigid so far as it goes, but of course, like all other physical methods, it is an approximation to the truth which can be carried out with any required degree of exactness. For example, I show that each element is characterised by 8448 constants; but this number is got by using the number 132, which is only the number of points through which the affinity surface is supposed to pass in my particular investigation. If we consider the relation of the elements to a smaller number of elements, we get a smaller number of constants; if more, we get a greater number. The greater the number of constants we use, the more exact is the description of the properties of the element, on the same mathematical principle, that the greater the number of points we take on a curve, the more exactly does the formula of the curve thus deduced correspond to its

actual figure. The number of constants employed in my particular investigations, namely, 8448, is enormously far in advance of the needs of present day chemistry, a mere 100 or 200 is probably more than enough for our in completely developed chemistry.

Another objection which may suggest itself to the reader is that our known elementary species may be in reality compounds. This, however, does not effect the fact that, whether they be compounds or not, the properties of the elements are governed solely by the affinities it exerts on them. In fact, it is explicitly stated that compounds as well as elements can be represented by characteristic surfaces.

Chap. I has already been published in an abstract form in the Chem. News (1904). **90**. 175.

Chapter VII, which treats of the variation in the properties of the elements with the temperature and pressure, is speculative and can be accepted or rejected according to the mental constitution of the reader. The chapter, however, has been very carefully considered, and my opinion has been formed not at all hastily, but gradually by the minute study, extending over years, of an immense mass of data. It is the logical outcome of the foregoing researches. Whether or not I have hit on the correct law, is at present impossible to say. But a law of some kind must regulate the variation in the properties of the elements, and it is an inherently probable suggestion, that the chemical condition a given element finds itself in under ordinary external physical conditions is a phase, which can be assumed by the other elements also, under other suitable external conditions, in the same way that the solid, liquid, and gaseous states are phases which can be assumed in succession by all bodies by properly choosing the external physical conditions under which they are viewed. At any rate, the alternate suggestion that the properties of elements remain absolutely invariable under all external conditions to which they can be subjected, is very much more improbable.

It may be noted that if our supposition is correct, living matter may exist on other planets composed out of entirely other elements than those which make up the living matter on this earth, on account of the different physical conditions holding on these planets, bringing about a transformation in the properties of elements which render them suitable for entering into the construction of living matter.

Chapter VII is composed out of a series of articles which appeared in the Chemical News October 14. **1904**; December 19. **1902**; February 13. 1903; April 3. 1903; June 29. 1900.

The 3 appendices at the end of the book, though not in direct connection with the matter contained in the work, were suggested to me by researches contained therein. In studying the stabilities of the various valency grade compounds of the elements I often had occasion to remark that an element often passes directly from one grade of combination to another, without producing compounds of intermediate grades of union. The explanation of this fact is I think, given correctly for the first time in appendix A and is due to the circumstance that the force an element A exerts when in a grade of valency N

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and also in a grade of valency $N-2$ is often greater than the force it exerts when in the grade of valency $N-1$. In appendix B I introduce a new conception, namely, that every chemical compound has a critical temperature and pressure of decomposition (just as it has a critical temperature and pressure of liquefaction and that protoplasm is nothing more or less than a compound whose critical temperature and pressure of decomposition coincides precisely with the temperature and pressure upon the earth. Some parts of the protoplasm decompose somewhat more rapidly than other parts, because they have somewhat different critical temperatures of decomposition. It is owing to this fact that the different activities and differentiation of the different parts of living matter are possible — some parts corresponding more sensitively to certain influences than others, and thus developing into different organs. It is then suggested that protoplasm has evolved from other kinds of protoplasm living at high temperatures, in which heavier elements replaced the lighter elements C, H, O, N, which now principally compose it. The whole is founded upon a series of articles which I published 5 years ago in a now defunct periodical "Science Gossip" (March, April, May, June, 1900) and in "Nature" April 27th. 1905 p. 608.

In appendice C, is discussed from this point of view the habit of alcohol drinking, and it is suggested that it may be the beginning of an organic tendency which will ultimately lead to the elimination of water in living matter, and its replacement by the more mobile alcohol, in order that as the temperature of the earth and sun falls the aqueous fluids in living matter may be replaced by alcoholic fluids which will remain liquid under conditions which convert water into a solid state.

It is indeed a very curious fact, which has never been adequately explained, that men seem to avoid almost instinctively the use of pure water as a beverage. They drink either tea, beer, or alcoholic liquids, but only water, when they are either very thirsty or when other liquids cannot be obtained. There must be some scientific cause underlying this tendency, and I think that appendix C opens out a very curious possibility as what this tendency may ultimately lead to.

For convenience we summarise briefly here the conclusions arrived at in the following pages.

- 1) An atom or radicle is chemically similar to another when, and only when, its affinities are proportional to those of the other. So that chemically similar elements have necessarily geometrically similar affinity curves or affinity surfaces. The more nearly equal, each to each, are the affinities the two elements exert, the more alike are they chemically.
- 2) If we compare the affinity surfaces (or curves) of the successive elements, they take the appearance of successive positions of an advancing wave, which repeats itself at the end of every fresh cycle of elements of the Periodic System; and that in consequence of this fact nitrogen possesses very powerful affinities for certain elements, and very feeble affinities for others, in precisely the same way that oxygen and chlorine have very powerful affinities for some and very feeble affinities for other elements; and that the prevalent notion of

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the great instability of all nitrogen compounds is quite incorrect. The great power of self-combination that carbon and silicon possess also arises from the same law.

- 3) That as a statistical result it appears that chemically unstable compounds are volatile and fusible; chemically stable compounds fixed and fusible with difficulty.
- 4) That compounds of a high valency grade are more volatile than compounds of a low valency grade.
- 5) That the molecular weight is of quite subordinate importance as compared with the nature of the atom in determining the volatility and fusibility of elements and compounds.
- 6) The researches incidentally throw light on the theory of solution, making clear why dissolved molecules should behave as if in a vacuum, why chemically similar substances should be miscible in all proportions, why solubility increases with the temperature, why there is a limit to solubility &c. &c.
- 7) That the same factors which determine the chemical properties of an atom also determine its physical properties.
- 8) That the properties of an element depend almost entirely upon the forces with which it attracts other elementary kinds of atoms; so that by representing these forces graphically we represent graphically all the chemical properties of the element. In consequence of this fact it is possible to reduce chemistry to a branch of applied mathematics because the magnitudes of the affinities an element exerts can be taken as the coordinates, which determine its properties in the same way that the magnitude of the coordinates of a point in space determine its position.

In consequence of this circumstance all changes in the properties of the element or compound can be expressed by an analytical expression (chap I and VI) which is the expression of the change in the values of the coordinates (ie. the affinities) which determine the properties of the element.

- 9) That the properties an element exhibits at ordinary temperatures and pressures are probably only a phase which other elements can also assume under other external physical conditions.

My conclusions are somewhat at variance with the current notions of chemists, and this will, perhaps, lay me upon to attack. My critics will find, however, that they are dealing with a prepared opponent, who will mast them on their own ground.

I should like here to express my indebtedness to Prof. Sydney Young, and Prof. James Walker for kindly consenting to read through part of the manuscript and for their valuable advice and criticism on the same. Also to Prof. J. Wertheimer of Bristol for reading through the proof-sheets and for valuable criticism and suggestions.

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Chapter I.

Method of describing the properties of an element by means of a Characteristic Surface.

7 § 1. Introductory remarks.

Every relationship which the human mind is capable of comprehending can be represented geometrically in some way or other.

If this relationship takes a form capable of being referred to number or subjected to measurement then it can be represented geometrically by a figure whose magnitude and shape measures numerically the degree of the relationship.

And since every geometrical locus is capable of being represented by an analytical expression, it follows that every relationship which the human mind is capable of comprehending is ultimately expressible by means of the symbols of a mathematical calculus.

As a manifestation of this peculiarity of the human mind we may mention the fact that when we follow the history of any science, we find that it invariably evolves stage by stage from a descriptive or qualitative, into a quantitative, and finally into a mathematical form.

In particular, the properties of elements are also relationships which must be capable in some way or other of being portrayed geometrically. And since these properties are, in general, subjectible to measurement, they must also be capable of being expressed quantitatively by an analytical expression which is the equation of the geometrical figure which pictures them.

The general problem which we propose to investigate, is the construction of some geometrical figure which will quantitatively portray the chemical properties of the element.

So that to every different element there will correspond a different figure; and by merely inspecting the shape of the figure corresponding to a particular element when viewed under particular conditions of temperature and pressure we will be able to predict quantitatively beforehand the effects the element will produce.

The equation of this figure will, in fact, bear the same relationship to that manifold of properties which is comprehended under the name of the element, as the equation of a curve bears to that manifold of geometrical points which is comprehended under the name of the curve.

For just as in the latter case all the geometrical properties of the curve can be deduced from the analytical expression which describes it, so in the former case all the chemical properties of the element can be deduced from the analytical expression of the geometrical locus which describes it. In order to do this we must first determine upon what factors depend the chemical properties of an element; and then we must devise some method of representing these factors geometrically. It is this which forms the subject of the present essay.

The solution of this problem would be of the very greatest importance; it would bring chemical science ultimately under the sway of mathematics as completely as Astronomy or Mechanics is now. All elements and compounds would be represented by mathematical expressions, and the most complicated changes in the chemical properties of elements with the temperature and pressure, such as is at the present time only expressible by a long descriptive account, would be represented in the simplest possible manner by changes in the form of the mathematical expression which represents their properties.

We have only to think, for example, of the almost impossibility of accurately describing descriptively all the changes in the properties of carbon, and its properties at any given

temperature instant, between the temperature of liquid hydrogen and that of the electric arc.

Yet if the properties of carbon could be represented by an analytical expression, or what is the same thing, by a geometrical curve or surface of which the analytical expression is the equation, we could follow with the greatest possible ease all the changes of properties, and also determine its properties at any given temperature instant, by simply following the changes in the shape of the geometrical locus which describes its properties.

It may be noted that the problem here set forth is merely an extension of the old idea of representing an element by means of a symbol. For example the symbol Cu stands for copper, but this symbol gives us no information whatever about the chemical properties of copper.

We propose to replace the symbol Cu by a mathematical expression which will stand for copper in the same way that the symbol Cu does but which will in addition express concisely and in a quantitative form the chemical properties of copper. In fact, we propose to replace the expressive symbols of chemistry by substitutive Symbols.

In organic Chemistry this has, partially at any rate, been already done. For the constitutional formula of a compound is nothing more or less than a short-hand method of writing out the it reacts.

But even this method is very imperfect, since by contemplating the constitutional formula of a compound, we cannot at once state with numerical precision, exactly how and to what extent the compound will react under definite conditions. The constitutional formula of a compound has in fact, only a qualitative value.

The invention of some method, such as we have pictured, of concisely expressing the properties of an element will sooner or later be forced upon the attention of chemists, if chemical science is to keep pace with the enormous mass of new facts yearly accumulating — most of which are theoretically deducible

beforehand from a knowledge of the exact nature and magnitude of the factors which determine the way an element reacts.

In this part we confine ourselves to the problem of the representation of elements by means of surfaces.

But compounds can also be represented by surfaces in a similar way.

§ 2. The elements have different affinities for each other.

The chemical unit is the atom. The various kinds of atoms do not remain free and isolated, but are driven by attractive forces to associate together to form complex aggregates known as molecules.

It is the play and interplay of these forces which lead to the arrangement and rearrangement of the groupings of the constituent atoms when systems of different molecules are brought into contact.

And thus it is the chemical attractions which different atoms exert on each other which are the direct underlying cause of all the changing phenomena of chemistry.

An atom has in general a greater tendency to combine with some atoms than with others. (In fact, did every atom attract every other kind of atom equally, then chemical change as we know it, would be impossible.) For example, hydrogen atoms have a great attraction for fluorine atoms and combine with them at ordinary temperatures with explosive violence; Oxygen atoms, on the other hand, have very little affinity for fluorine atoms and cannot be made to combine with them.

Every elementary species of atom, in fact, exerts on any given species of atom a definite intensity of attraction which can be given a definite numerical value.

If this attraction is very great the two species of atoms combine together to form stable compounds; if small they combine to form unstable compounds, or perhaps do not combine at all.

In general the intensity of the attraction which the atoms of such an element as oxygen exert on an atomic species A may be estimated very roughly by the ease or difficulty with which the oxygen can be removed from its combinations with that atomic species. For example, PbO is easier to reduce to Pb than InO to In; and harder to reduce to Pb than HgO is to reduce to Hg. We hence conclude that O attracts Pb with a smaller intensity of force than it attracts In; and with a greater intensity of force than it attracts Hg. Similarly it is easier to remove all the chlorine from Pt Cl_4 so as to reduce it to Pt than it is to remove it from Cr Cl_3 so as to reduce it to Cr. Hence Chlorine is attracted by Pt atoms with a feebler intensity of force than it is attracted by Cr atoms.

It is therefore possible by examining the stability of the oxides or chlorides of the elements to arrive at an opinion as regards the intensity of the different forces with which oxygen and chlorine attracts the different elements. Such a study, however, fails to give us more than a qualitative notion of the affinity of the elements for each other. In fact, every attempt yet made (notably Julius Thomsen's) to give a numerical value to the affinities have broken down, yet such values must exist. To see this let us imagine we take a single atom of (say) Oxygen, and hold it by some means fixed in space. Now let us bring up to within a very small unit distance from it a single atom of another element (say lead). Then the O atom must exert on the lead atom at this distance a definite attraction which (did we only possess experimental skill enough) could be measured in dynes, and which may be defined as the „specific attraction“ of O for Pb. Suppose now we substitute for the lead atom another atom, say an aluminium atom, keeping as before the distance constant.

Then the oxygen atom will now exert a different (and more intense) attraction on the aluminium atom, which likewise is expressible in dynes, and which would measure the specific attraction of O for Al.

By knowing the law according which the force between the two atoms decays with the distance between them (a law

at present not known with certainty, but which will some day be discovered), the attractive force could be calculated at any given distance; so that all we require to completely determine the force exerted by one atom on the other at any given distance, is its „specific attraction“, and the law of decay of force.

Atoms thus possess a definite specific attraction for each other. But since this specific attraction probably alters with the temperature, medium, &c. we must be careful to define the conditions under which the atom is viewed before we speak of its „specific attraction“.

Every chemist, I believe, within the last 100 years has been compelled to admit that such chemical forces exist, which are more intense for some elements than for others. It is true, that at present all attempts to gauge the absolute magnitude of these forces have broken down. But there is no reason to doubt that sooner or later chemical science will advance to such a point that these magnitudes will be determined in dynes numerically. For example, within the last 50 years, we have discovered means of measuring roughly the absolute magnitudes of the atoms, and even of determining approximately their absolute shape. I think, that it is surely not going too far to imagine that in a few years time we will be able to determine the actual forces which an atom exerts on atoms of other kinds, when at a small known distance from them. When this is achieved, each different atomic species will be characterised by these numerical forces in the way set forth below.

§ 3. The chemical properties of an element depends entirely upon its chemical affinities.

The chemical properties of elements depend entirely upon the intensity of the chemical forces with which their atoms attract other atomic species. For these are the forces which decide with which elements a given element will react, its degree of

chemical activity, the stability of the compounds it produces, and to a very great extent their fusibility, solubility, volatility, hardness &c, as we will presently show.

A formal proof of the dependence of the chemical properties of an atom upon its chemical affinities may be given as follows. Consider two different atomic species A and B. And suppose A attracts the n different elementary atomic species with the n different forces

$$f_1, f_2, f_3 \dots \dots \dots f_n.$$

And suppose that the same forces for B are

$$f_1', f_2', f_3' \dots \dots \dots f_n'.$$

Then if

$$f_1 = f_1'; f_2 = f_2'; f_3 = f_3' \dots \dots \dots f_n = f_n'.$$

B will produce the same chemical effects as A, and hence may replace it in a reaction without altering the course of the reaction. For since B now exerts chemical forces of precisely the same intensity as A, then when A is capable of uniting with an atom C to produce AC, B will also under the same conditions unite with C to produce BC; and since C is attached both to A and to B with precisely the same intensity of force, any influence which is capable of tearing away C from A in AC will also be capable of tearing away C from B in BC, and thus bring about a change in both compounds simultaneously; moreover the chemical change will be a similar one in both cases; for since each of the atoms A and B exercise the same attractive power on the same atoms or group of atoms, it follows that when in the compound AC the C is by a given operation replaced by another atom or atomic group X, so as to produce the compound AX. then necessarily also in the compound BC, the C will also be removed by this same influence and in its place will be substituted the same group X which will be held by both A and B with the same intensity of force.

Thus the two compounds AC and BC will always react chemically in the same way when exposed to the same influences.

For a similar reason the resulting compounds AX and BX will always react in the same way; so that to every possible compound AC capable of being produced under any given conditions by A, there will correspond a compound BC capable of being produced under the same conditions by B, which two compounds will invariably react in the same way.

B therefore will be capable of producing the same chemical effects as A, and hence may replace it in any given reaction without in the least altering the nature of the reaction. So that A and B are chemically similar atomic species — such, for example, as Na and K.

It may be noticed that A and B may differ very largely as regards the magnitude of their atoms and yet produce the same chemical effects provided that:

$$f_1 = f_1'; f_2 = f_2'; f_3 = f_3'; \dots \dots \dots f_n = f_n'.$$

For example the Cs and Li atoms produce very similar chemical effects, and yet the Cs atom is 19 times heavier than the Li atom. The magnitude of the atomic weight, in fact, has little or nothing to do with chemical similarity. Nor is it necessary that in the two compounds AC and BC the same number of C atoms are united with a single atom of A and B. For example BCl_3 and SiCl_4 are chemically similar, and yet the one contains 3 atoms of Cl. and the other 4 atoms of Cl united with a single atom of B and Si respectively. Similarly WO_3 and Fe_2O_3 are chemically similar. The factor which determines the chemical similarity of elements is, in fact, not their valence nor the magnitude of their atoms, but their capacity for exerting an attractive force of the same intensity, or of a proportional intensity, on the same atoms or radicles as we shall later see in the next chapter.

If however the system of forces which A exerts be not equal to the corresponding forces which B exerts, then A cannot be replaced by B, for B will cause different chemical reactions from A, combining with some elements with which A is not capable of combining with because it attracts them more strongly than A does, and not combining with some elements which A can combine with, because it attracts them less strongly than A does.

So that B will be able to cause reactions which A cannot cause, and conversely A will be able to cause reactions which B cannot cause.

And the more do the system of A forces differ in intensity from the corresponding B forces, the more will A and B differ from each other in the way they react; moreover even when the two elements combine to produce the two compounds AC and BC, then if C is attracted by A less strongly than by B, any influence which is capable of removing C from A, will not in general be capable of removing C from B, so that the two compounds AC and BC will not in general be capable of reacting in the same way.

And since this holds for any pair of corresponding compounds AC and BC producible by A and B, the set of compounds producible by A will in general not react in the same way as the corresponding set of compounds producible by B.

And the difference in the way which the compounds of A and B react will become more and more pronounced according as the A forces differ more and more from the corresponding B forces. It is clear therefore, that the forces with which the atoms of an element attract, other elements completely determine the way in which the element reacts. And hence when these forces are known it is theoretically possible to completely predict the chemical effects producible by an element under definite conditions.

If, therefore, we can devise any geometrical figure which will accurately represent these forces, we will at the same time construct a figure which will accurately picture all those properties of the element which depend upon the chemical forces it exerts. And from a minute inspection of this figure we will be able to predict beforehand the exact chemical effects the element is capable of producing.

That the volatility, fusibility, solubility, hardness, of different elements and compounds depend to a very great extent upon these same forces appears from the following considerations.*)

*) Chem. News. May 29. 1904.

Compounds and elements which react in a very similar way with different reagents usually approach each other very closely as regards volatility, fusibility, hardness, solubility &c.

For example HCl, HBr, HI, are all chemically similar and all volatile enough to be gaseous at ordinary temperatures, though the molecule of HBr is more than twice as heavy as the molecule of HCl, and that of HI nearly four times as heavy. They are also in general soluble in the same reagents.

Similary BCl_3 , SiCl_4 are both volatile liquids; B_2O_3 , SiO_2 are both fixed solids; KCl, NaCl both soft solids &c. &c.; F_2 , Cl_2 , Br_2 volatile gases; Boron and Silicon fixed solids &c. &c.

I think that the general truth of our observation will be apparent to everyone who has even a superficial knowledge of Chemistry.

Now the chemical similarity of two compounds (or elements) arises from the equality of the intensity of the chemical forces at play within the molecule. For example, SiCl_4 and BCl_3 are chemically similar because:

- a) Both B and Si attract Cl with nearly the same intensity of force.
- b) The B and the Si attract other radicles also with nearly the same intensity of force.

For when the first condition is fulfilled, any influence which is capable of removing the Cl from the one molecule will be capable of removing it from the other;

and when the second condition is fulfilled, the B and the Si will enter into the same reactions.

So that the two molecules BCl_3 and SiCl_4 will, when subjected to the same influences, react in the same way.

That as a matter of fact, in BCl_3 and SiCl_4 the Cl is attached to the B and the Si atoms with nearly the same intensity of force appears from the thermal data:

$$\frac{1}{3} (\text{B}, \text{Cl}^3) = 34,6 \qquad \frac{1}{4} (\text{Si}, \text{Cl}^4) = 39,4$$

And that B and Si attract not only Chlorine, but other radicles as Oxygen, with nearly the same force appears from the data:

$$^{1/6} (B^2, O^3) = 52,8$$

$$^{1/4} (Si, O^2) = 52,7$$

And that chemically simular atomic species in general owe their chemical similarity to the fact that they in general attract the same radicles with nearly the same intensity of force likewise appears from a study of thermo-chemical data (for exact theory see next chapter).

For example, cobalt and nickel attract the same radicles with nearly the same intensity of force, as appears from the following thermal data :

Reaction	Co	Ni
$R + Cl_2 + Aq$	95	94
$R + Br_2 + Aq$	73	72
$R + O + Aq$	63	61
$R + O_2 + SO_2 + nH_2O$	163	163
$RCl_2 + Aq$	18	19

R stands for either nickel or cobalt; the numbers are the heat evolved by the corresponding reactions (Thomsen).

The fact that chemically similar compounds possess nearly the same degree of volatility, fusibility, hardness, solnbility &c., is almost certainly connected with the fact that the chemical forces at play within their molecules are nearly of the same intensity.

It seems therefore that it is the internal chemical forces which the atoms exert on each other in the molecule which decides the external attractive force with which the molecules themselves are attracted together, and therefore the volatility, fusibility and hardness of the compound.

The mere magnitude of the molecular weight has very little influence as compared with the influence of the chemical forces in deciding the volatility or hardness of compounds or elements.

For example, compounds and elements composed out of very light molecules are often enormously less volatile and harder than compounds and elements composed out of very heavy molecules,

because the light molecules attract each other with a greater intensity of force than the heavy molecules do.

For example the molecules of OsO_4 weigh 255, and the molecules of Na only 23; yet OsO_4 is enormously more volatile than Na. Compare also H and He, O and F, Hg and Mg, UCl_3 and UCl_4 &c &c. In all these cases the heavier molecules are the more volatile. In fact, the influence of the molecular weight on the volatility only becomes apparent when we eliminate the effect of the chemical forces by considering chemically similar compounds or elements (i. e. compounds or elements in which the chemical forces are of nearly the same intensity). When we compare chemically dissimilar compounds or elements (i. e. compounds or elements in which the chemical forces at play are of very different intensities), the influence of the molecular weight entirely disappears, and the chemical forces alone decide the volatility.

For example, the replacing of hydrogen in the molecule by Cl or F (atoms 35,5 and 19 times heavier than H) sometimes leads to an increase of volatility, although the molecular weight is thereby greatly increased [Henri. Rec. Trav. Chem. (1897) XVI. 218, 225], e. g.:

CHCl_3 boils at 61°C	CH_2Cl_2 boils at 41°C
CFCl_3 24°C	CHFCl_2 boils at $14,5^\circ \text{C}$
$\text{NC.CH}_2\text{Cl}$ boils at 123°C	
NC.CHCl_2 boils at 112°C	
NC.CCl_3 boils at 83°C	

And this is so with the solubility also. In general it is not those compounds or elements which approach each other nearest as regards the magnitude of their molecular weight which approach each other nearest as regards their solubility; instead it is precisely those substances which approach each other nearest in the way they react which approach each other nearest as regards their solubility; so that the solubility must also like the volatility, fusibility, solubility, hardness &c of any given compound or element, depend almost entirely upon the intensity of the chemical forces with which the atoms which compose it attract other atomic

species, and that did we only know the exact intensity of these forces, and the law governing the relationship between them and the intensity of the resultant molecular attraction, it would be possible to calculate mathematically the volatility, solubility, hardness &c, of the compound or element — a definite correction being necessary for the gravitational influence of the magnitude of the molecular weight.

The elements are only compounds in which the atoms of the molecules are of the same kind; eg. O_2 and O_3 are two different compounds composed of atoms of the kind. Consequently the same laws which apply to compounds in general apply to elements in particular. Therefore the volatility, fusibility, solubility, hardness &c of the elements themselves in general depend mainly upon the intensity of the forces with which their atoms attract other atomic species, and to a very much smaller extent upon the magnitudes of their atoms and molecules — as indeed is evident from the Periodic Law, which states that if the elements are arranged in the order of their atomic weights the series does not exhibit one continuous progressive modification of the physical and chemical properties of the successive elements (as it should do if the intensity of the chemical attraction increased or diminished continually with the atomic weight) but that similarities reoccur at stated intervals in the series. A knowledge of these forces would, therefore, give us a very complete picture not only of the chemical, but also of the physical properties of the element; and hence any method of representing these forces graphically will give us not only a complete picture of the chemical properties of the element but also a fairly complete picture of the physical properties of the element as well.

So that the problem we have set out with, namely the representation of the properties of an element by means of a geometrical figure would then be solved theoretically.

Before proceeding to construct this figure we must make a few remarks of general importance.

§ 4. An element can be imagined to be replaced by a system of attractive forces which will produce all the results producible by the element itself.

Chemically an element makes its presence known by the chemical effects it produces on other kinds of matter — in other words, by its chemical properties.

And as we have seen these properties are decided by the attractive forces which its atoms exert on the atoms of other kinds of elementary matter.

For our present purpose we may abolish altogether the idea of the corporality of an element or compound and think of it as consisting only of the system of attractive forces § 2 acting at a point in space, namely of the n different forces which it exerts on the n different elements.

The chemical effect produced by such a system of attractive forces would be precisely the same as that produced by the atom or compound if at the point whereat these forces act; for example, consider an atom of an element in a material system — eg. an atomic structure of any kind.

The stability or otherwise of this structure is due to the interaction of the affinities holding it together.

If the atom be imagined removed and its place be taken by a system of attractive forces precisely equal in every respect to those which the atom formerly exerted when at this point, no change whatever would take place in the material system but it would continue in its state of rest or motion, internal and external, precisely as if the atom was still present,

The system of attractive forces which have thus taken the place of the atom would simulate in every respect the effect producible by the atom when at this point.

Moreover if there be x different atomic species present in the structure there will be x different forces which the atom A exerts on the x different atoms.

So that the replacing of A by the system of attractive forces $f_1, f_2, f_3 \dots f_n$ considered in § 2 will produce the same effects as A , since every different atom will be attracted by

the force proper to it, because in this system there are as many different attractive forces as there are different atomic species — those atoms which are absent being regarded as at an infinite distance.

It may be noted that we are here but extending the application of Newton's third law of Motion to those very small particles of matter called atoms, and thus are making the generalisations of Newton apply not only to matter in the stellar universe, but also to that smaller universe of which atoms are the constituent parts.

Newtons third law of Motion declares that „action is also associated with reaction and is equal to it“.

Applying this to those systems of atoms which are held together by the attractions they exert on each other, we at once see that it is possible to, so to speak, displace the individual atoms themselves by the forces they exert. This is done in almost every problem in ordinary dynamics, the method being first introduced by the great French mathematician D'Alembert, and is now known by his name. And there is no reason why we should not extend D'Alembert's Principle to those systems of matter particles called molecules and erect on this basis a mathematical Chemistry.

An element can be represented geometrically by a surface.

We now proceed to represent graphically these forces and thus to represent graphically the chemical properties of an atom. Just as the position of a point in an n -dimensional space is completely determined when we know the magnitudes of its n -coordinates, so also the chemical properties of an element are completely determined, when we know the magnitudes of its n affinities $f_1, f_2, f_3, f_4 \dots f_n$.

In this sense we may call these n forces the n -co-ordinates of the atom.

Were we dealing with an n -dimensional space, we could regard these n magnitudes as fixing the position of a point in this space; and the point could be taken as completely representing the element, since knowing the position of the point we know the magnitudes of the affinities of the element and hence its properties.

Moreover the variation in these attractive forces (the co-ordinates of the element) with the temperature and pressure, would cause this point to describe a curve, which would express the change in properties which the element undergoes with the temperature and pressure.

Dealing however with a three dimensional space, we may take these n magnitudes as determining n points upon a surface in the manner we will presently describe.

And the surface which is thus decided by these n points will express if suitably interpreted, completely the chemical properties of the element.

The variations with the temperature in the intensity of these forces will be expressed by variations in the position of the n points in space.

So that all the fluctuations in the properties of an element with the temperature and pressure are completely represented by corresponding fluctuations in the shape of the surface.

We now proceed to describe this surface.

Construction of the characteristic surface.

Imagine the Periodic System of the elements to be plotted out on a flat surface, as follows (see fig. 1):

The group numbers are plotted along OX and the series numbers along OY.

Then the position of any element may be represented by a point, which is completely known when its x and y co-ordinates are known; for example the point

$x = 1, y = 2$ represents Li

$x = 5, y = 6$ represents Nb

$x = 4, y = 4$ represents Ti.

Suppose now we take any given atomic species A whose characteristic surface it is required to construct, and measure the attractive force which it exerts on the atoms of the various elements of the Periodic System.

And let us erect a perpendicular from every point in the previous diagram (fig. I) of a length proportional to the attractive force which A exerts on the element represented by that point.

Now imagine a surface to be described through the summits of these perpendiculars.

Then this surface is the required characteristic surface of the atomic species A.

This surface may be represented by an equation:

$$F(x, y, z) = 0$$

where

x is the group number of any element in the Periodic System,

y the series number of the same element,

z the attractive force exerted by the element A (whose characteristic surface it is required to construct) on the element x, y .

Solving for z :

$$z = \Phi(x, y)$$

Substituting x', y' für x, y in this equation we obtain this attractive force for any other element x', y' of the Periodic System. And thus by substituting successive integer values of x and y , — corresponding to the successive elements of the Periodic System — we obtain the successive values of the attractive forces which A exerts on the successive elements of the Periodic System.

To every element A, therefore, there may be ascribed an algebraical equation $F(x, y, z) = 0$ from which can be deduced the attractive force it exerts on any elementary atomic species whatever.

So that given this equation of the characteristic surface we can deduce therefrom the n affinities of the element and thus all those properties which depend upon these affinities.

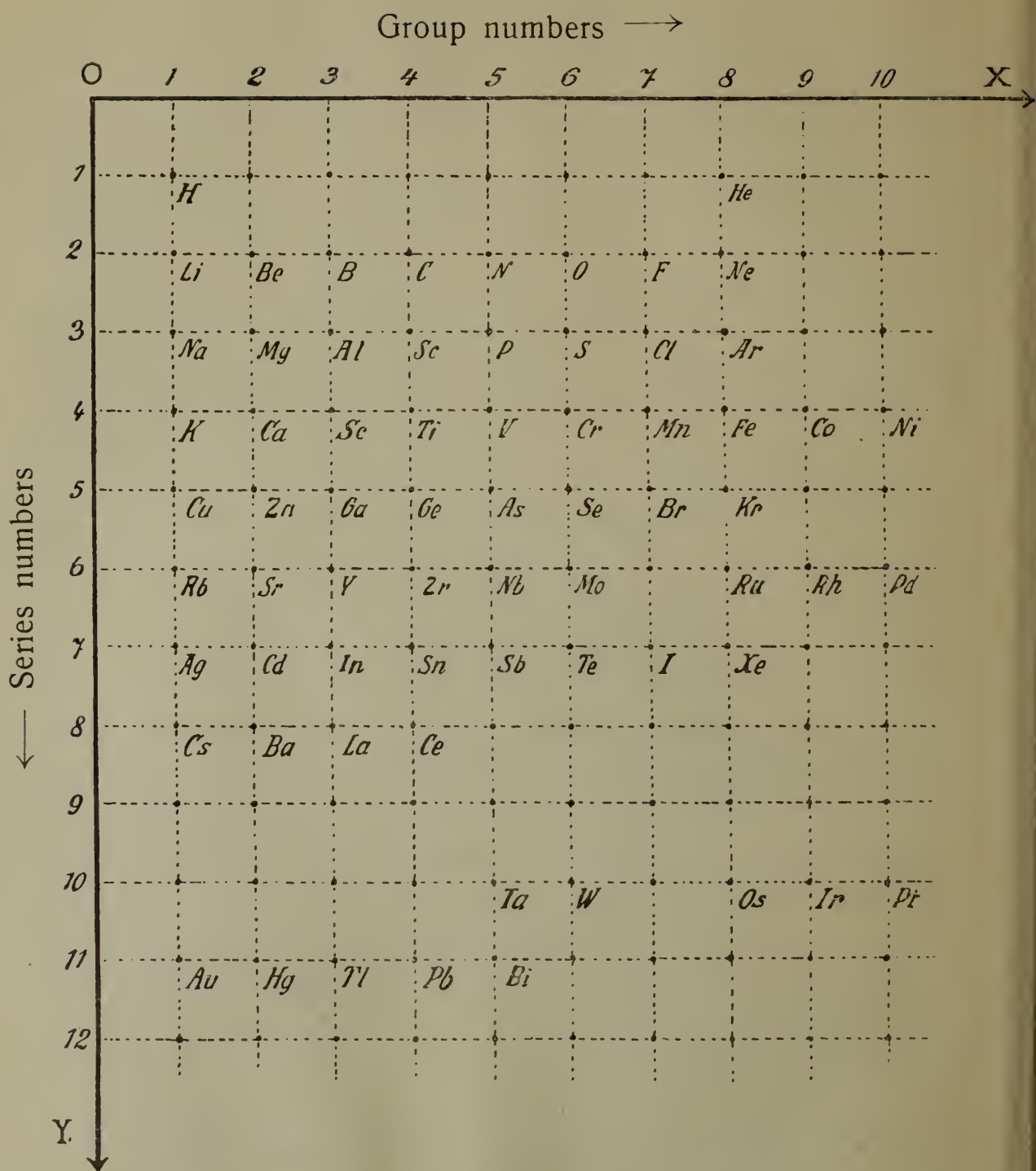


Fig. 1.

Showing how the position of an element is fixed by its x and y co-ordinates, x being the group number of the element, and y the series number in Mendeléeef's Periodic System.

Hence this equation when suitably interpreted represents in a quantitative form the chemical properties of the element; and reasoning about the element may be replaced by reasoning about this equation.

In fact the equation of the characteristic surface of an element bears the same relation to the element as does the equation of a curve bear to the curve.

For in the same way that the geometrical properties of a curve are deduced from its equation by giving successive values to the variables x and y , so also in a precisely similar manner are the chemical properties of the element derived from its characteristic equation.

For a reason that will hereafter become plain, we will speak of the surface just described as the Affinity Surface, reserving for a collection of such surfaces the name Characteristic Surface.

Determination of the equation of the affinity surface.

By referring to fig. I it will be seen that there are in all $11 \times 12 = 132$ different points through which the affinity surface is supposed to pass.

This, therefore, must be the number of conditions which the surface must satisfy. The equation of the surface must contain in all one term more than the number of conditions it must satisfy viz 133 terms.

Again

1. a perpendicular to the plane XOY can only cut the surface in one point, because every element is supposed to attract the element whose affinity surface is being constructed with only a single force. Hence the equation of the surface can contain z (the attractive force) in the first degree only.
2. a straight line drawn parallel to OX can in the most favourable case cut the surface in 10 different points, because the attraction z can sink or rise as we pass from one element to the other, and there can exist in all 10 different elements along a line parallel to OX. Consider, for example, the series of elements K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni. Then as we pass from the point 0,4 to 1,4 (ie from 0,4 to K), the attraction rises from zero at 0,4 (because no element exists at 0,4) to a

definite value at 1,4. Hence the line parallel to OX can intersect the surface in one point between 0,4 and 1,4. Suppose now the attraction sinks from K to Ca (from 1,4 to 2,4), then the line can again intersect the affinity surface. So that the line now intersects the surface in two points; and so on, an additional point of intersection being added on for every element we consider. And there being in all 10 elements in the row, there are in all 10 possible intersections.

Hence the equation of the surface can contain x in the 10th degree.

3. Similarly a straight line drawn parallel to OY can cut the surface in the most favourable case in at least 11 points and hence can contain y in at least the 11th degree.

The problem then reduces to constructing an equation of 133 terms; containing x in the 10th degree, y in the 11th degree, and z in the first degree — the following is an equation of this form:

$$\Phi(x, y) + z = 0 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $\Phi(x, y)$ is of the form:

$$\begin{aligned} & a_1 y^{11} + a_2 y^{10} + a_3 y^9 + \quad . \quad . \quad . \quad . \quad + a_{11} y \\ & + b_1 x^{10} + b_2 x^9 + b_3 x^8 + \quad . \quad . \quad . \quad . \quad + b_{10} x \\ & + y^{11} (b_1' x + b_2' x^2 + b_3' x^3 + \quad . \quad . \quad + b_{10}' x^{10}) \\ & + y^{10} (b_1'' x + b_2'' x^2 + b_3'' x^3 + \quad . \quad . \quad + b_{10}'' x^{10}) \\ & + y^9 (b_1''' x + b_2''' x^2 + b_3''' x^3 + \quad . \quad . \quad + b_{10}''' x^{10}) \\ & + \quad - \quad - \quad - \quad - \quad - \quad - \quad - \quad - \quad - \quad - \quad - \quad - \quad - \\ & + \quad - \quad - \quad - \quad - \quad - \quad - \quad - \quad - \quad - \quad - \quad - \quad - \quad - \\ & + y^2 (b_1^x x + b_2^x x^2 + b_3^x x^3 + \quad . \quad . \quad + b_{10}^x x^{10}) \\ & + y (b_1^{XI} x + b_2^{XI} x^2 + b_3^{XI} x^3 + \quad . \quad . \quad + b_{10}^{XI} x^{10}) \\ & + K. \end{aligned}$$

Where $a_1, a_2, a_3 \quad . \quad . \quad . \quad b_1, b_2, b_3 \quad . \quad . \quad . \quad K$ are constants.

$\Phi(x, y)$ is therefore an expression containing $11 + 10 + 11 \times 10 + 1 = 132$ terms. So that (1) will contain in all 133 terms, and is therefore of the correct form.

By now substituting in succession in (1) the 132 supposed known different sets of values of x, y, z, we obtain 132 different

equations wherefrom to determine the 132 different constants, $a_1 a_2 a_3 \dots b_1 b_2 b_3 \dots K$ in (1).

So that by solving simultaneously those equations, every constant can be obtained in the form of a determinant divided by a determinant.

By now substituting in (1) the proper values of the constants thus determined, we obtain the analytical expression of the affinity surface of the particular element A.

It may be noted, that where there exists in Fig. (1) no real element corresponding to a given value of x and y (for example, along OX and OY), we simply put the attractive force z equal to zero (for if no element exists at a given point it can exert no attractive force); in the case of the elements of the helium group the attractive forces also seem to be almost zero, since these bodies seem to exert no perceptible chemical forces on other elements.

In practice, when we seek to carry out this determination of the equation of the affinity surface of an element, we meet with serious difficulties. In many parts of the Periodic System elements are entirely wanting, in others the elements are so rare and imperfectly known that we have no reliable data for judging of the affinities they possess for other elements. To overcome such difficulties we must resort to interpolation. We determine, for example, precisely as above the equation of a surface which passes through the summits of the perpendiculars which represent the affinities of known and well investigated elements.

We then find from this equation the affinity z for any other element x, y (whose affinity is unknown) by substituting the coordinates x, y , in the equation. In general, this will give us an approximately correct value of the affinities of x, y , because the Periodic Law shows that the properties of any element in a group x and series y are intermediate between those of the elements which come before and after it in the group and in the series; and are thus determinable by interpolation. In fact Mendeléef was able to predict with remarkable precision the properties of certain unknown elements by merely examining the properties of the neighbouring elements.

We thus get a new point, x , y , z through which the surface passes. We then repeat the whole process of finding the equation of the surface passing through this new point and the other points previously considered. And thus obtain a wider and more accurate expression for the affinity surface, which in its turn can be utilised in the same way.

Complication introduced by the fact that the attractional forces exerted by elements change with their valence.

We have hitherto supposed that a given atom A always exerts under definite temperature and pressure conditions a definite force upon other elements.

So long as an element remains in one particular valency state this is true.

Unfortunately however when an elementary atom enters into another valency state, in general it changes the force with which it attracts other atoms.

In general (though not always) an element in a low grade valency state exerts attractive forces of a higher intensity than when in a high-grade valency state.

For example, chlorine is but feebly attracted by lead when in a tetrad state — PbCl_4 being a very unstable body;

In a diad state, however, it is attracted with a very considerable force PbCl_2 being a very stable body.

If now in the case of any given element A , we measure the forces it exerts on other elements when in its different valency states, and construct therefrom affinity surfaces, one corresponding to every different valency grade, we would find that the surfaces corresponding to low grade valency states lie in general outside the surfaces corresponding to high grade valency states (because the attraction for other atoms is greater for low grade than for high grade valences).

Hence instead of there existing a single affinity surface for any given element, there exists a set of affinity surfaces, one corresponding to every particular valency state assumable by the element.

Most elements can assume a number of different valency states. Indeed probably an element can assume every valency state under suitable conditions; and that we are unaware of these hitherto unattained valency states because most elements are viewed under normal conditions of temperature and pressure. So that the only valency states of an element with which we are acquainted, are merely those which are most stable under normal temperatures and pressures.

By viewing the element, however, under other conditions of temperature and pressure, these known valency states may become unstable, and the unknown states stable.

So that by successively altering the conditons of temperature and pressure (and especially the medium in which the element is immersed) under which the element is viewed, we would bring successively into prominence all the grades of valency capable of being assumed by the element.

The sets of affinity surfaces corresponding to any given element would thus continually alter with the temperature and pressure and medium.

And the relative position of these affinity surfaces would give a picture of the relative degrees of stability of the various grades of valency compounds producible an element. We will call each of these single surfaces, an „Affinity Surface“ corresponding to a particular valency grade. But the complete collection of these surfaces we will call the „Characteristic Surface“ of an element, since the latter presents a complete picture of the properties of an atom, as we will immediately see.

Complete characteristic surface.

We will enter somewhat more closely upon the general theory of these valency affinity surfaces.

There are spaces in the Periodic System plotted in Fig. I for 120 elements, of which 67 are actually known.

In order to develop the theory we must introduce the principle of continuity and consider that every element can assume every grade of valence from 1 to 8 and perhaps higher. This is very probably really the case, though as a matter of fact when an elementary atom is physically incapable of existing in a given valency grade, we will for convenience imagine that it can exist in this grade, but that the compounds it produces are of zero stability, and thus are incapable of existing. So that we must for every valency grade which is not capable of being assumed by the element, merely consider the element to exert zero attractive force when in this grade of valency. The highest known grade of valency is 8 in (OsO_4 , $\text{Ni}(\text{CO})_4$ &c.) and in every one of these different valency states the element, in general, exerts a different attractive force on a given atom or radicle.

It follows, then, that to any one valency grade in which the element A (whose characteristic surface is to be constructed) can exist, there exist in general 8 different values of z (the attractive force) exerted on it by any given element x , y of the Periodic System — viz. the 8 different attractive forces corresponding to the 8 different valency grades in which the element x , y can exist.

But A in general can exist in at least 8 different valency grades. Hence the total number of different attractive forces which can exist between A and any given element x , y is at least $8 \times 8 = 64$.

Consequently the substitution of the co-ordinates x , y of an element in the equation of the complete characteristic surface of A will give in general at least 64 different values of z .

So that the complete characteristic equation of A will be at least of the 64th degree in z .

Now in general an almost unlimited number of affinity surfaces can be constructed for any given element A, by taking into

account all the different ways of associating the different valency grades which can be assumed by the various elements of the Periodic System.

For example, there exist places for 120 different elements in fig. 1, each of which can (at least theoretically) exist in at least 8 different valency grades; and the total number of ways which these different valency grades can be associated together is $8^{120} = 2,3486 \times 10^{108}$.

And this is the total number of affinity surfaces which can be constructed for a given element A.

We must therefore introduce some device in order to reduce the number of affinity surfaces and yet to completely picture the properties of the element.

We can by a suitable device reduce the number to 64, thus: Assume the element A to be in any given grade of valence n . And assume all the other elements to be in the grade of valence 1. Measure now the force which the element A when in the valency grade n exerts on all the other elements when in the grade of 1, and plot in this way an affinity surface whose equation may be conveniently written:

$$F_1 (x_1, y_1, z_n) = 0$$

where the suffixes x_1, y_1 denote that all the elements x, y of the Periodic System are in the grade of valency 1, while z_n shows that the element A is in the valency grade n . Suppose now all the elements to be in the grade of valency 2, and again plot the affinity surface for A the valency of A being supposed to remain constantly n .

And we get a new affinity surface:

$$F_2 (x_2, y_2, z_n) = 0$$

and so on for all the different grades of valence from 1 to 8 assumable by the elements.

Hence corresponding to the grade of valence n assumable by A there exist 8 different affinity surfaces, viz:

$$F_1(x_1, y_1, z_n) = 0$$

$$F_2(x_2, y_2, z_n) = 0$$

$$F_3(x_3, y_3, z_n) = 0$$

• • • • •

• • • • •

$$F_8(x_8, y_8, z_n) = 0$$

But A can exist in any grade of valence from 1 to 8, and to every one of these different valency grades there exist 8 affinity surfaces, making in all 64 different affinity surfaces corresponding to any given element A.

Hence the complete characteristic equation of A may be written thus:

$$F_1(x_1, y_1, z_1), F_2(x_1, y_1, z_2), F_3(x_1, y_1, z_3), \dots, F_8(x_1, y_1, z_8)$$

$$F_9(x_2, y_2, z_1), F_{10}(x_2, y_2, z_2), F_{11}(x_2, y_2, z_3) \quad . \quad F_{16}(x_2, y_2, z_8)$$

$$F_{17}(x_3, y_3, z_1), F_{18}(x_3, y_3, z_2), F_{19}(x_3, y_3, z_3) \quad . \quad F_{24}(x_3, y_3, z_8)$$

.....

• • • • •

$$F_{49}(x_7, y_7, z_1), F_{50}(x_7, y_7, z_2), F_{51}(x_7, y_7, z_3) \dots F_{56}(x_7, y_7, z_8)$$

$$F_{57} (x_8, y_8, z_1), F_{58} (x_8, y_8, z_2), F_{59} (x_8, y_8, z_3) \quad . \quad F_{64} (x_8, y_8, z_8)$$

$$= 0.$$

It is well to notice what we have accomplished here.

We have constructed the equation of the complete characteristic surface of any element A, which portrays quantitatively how the element reacts, in what grade of valence it comes to rest under given conditions, the relative degrees of stability of its different valency compounds &c, &c.

This equation in fact is a complete picture of all those properties of the element which depend upon the attractive forces the atoms exerts and of the various sets of valency compounds it is capable of producing.

It may be noted that the equation is one of very great complexity. Each affinity surface of the characteristic surface possesses 132 different constants.

So that corresponding to the 64 distinct affinity surfaces which make up the characteristic surface, there exist $64 \times 132 = 8448$ distinct constants to be measured — data which in the

present state of chemical science are for the most part completely wanting.

In the present state of science the preceding theorem only possesses a theoretical value. But from a theoretical standpoint it is surely a matter of great importance to be able to demonstrate that the properties of an element can be represented by a surface whose equation gives all these properties in a numerical form.

For the theorem gives us the means of treating an element by rigid mathematical methods, such as are at present entirely wanting. And some day when sufficient data exists it will become of practical importance, for it will enable us to discuss quantitatively questions of such difficulty that it is hopeless to attempt to discuss them by the methods now in vogue in chemistry.

It must be remembered that the whole of mathematics consists in the organisation of a series of aids to the imagination in the process of reasoning. In fact, the object of mathematics is to save imaginative thought, by transferring the reasoning from the things themselves to the substitutive symbols which stand for them.

Dalton's demonstration (which followed from the invention of the atomic theory) that it is possible to represent every element by a single symbol was the first step in this direction in chemistry.

Our demonstration that the properties of an element can be represented by a finite mathematical expression is an invention of a precisely similar nature.

It should be remembered that the demonstration that something is theoretically possible or impossible (quite apart from the practical difficulties of the scheme) is always of great importance.

For example we need only think of the importance of Abel's theoretical demonstration that it is impossible to solve algebraical equations of a higher degree than the 4th. And of the importance of the general mathematical demonstration that if we are given n linear independent relations connecting n variables, we can always determine absolutely each one of the n variables — a general theorem upon which Gibbs Phase Law rests.

My stand point is this: I prove that there exist for any element some $132 \times 64 = 8448$ constants which completely characterise it; and that from these can be deduced quantitatively every conceivable compound and every conceivable reaction which the element can give rise to.

It is true, I do not know the absolute magnitude of these constants. All that I know is that they exist and can be experimentally determined. When the practical chemist determines these constants for me, I will be able to substitute them in my mathematical expressions and accurately deduce the properties of the element — in the same way that we can accurately fix the geometrical properties of a curve when we know enough points on it.

At present the practical chemist cannot determine (merely on account of lack of experimental skill) these constants for me.

And therefore I cannot determine for him all the properties of the element. But this will not always be so. Some day the practical chemist will determine these constants; and then I, in my turn, will be able to theoretically predict with quantitative exactness every conceivable compound and every conceivable reaction which the element will produce, together with the exact degree of stability of the compounds, whether capable of higher oxidation &c. &c. That is surely a very important theoretical advance.

There can be little doubt that a complete investigation of the affinity surfaces corresponding to any particular element would bring most interesting results to light.

We may mention, for example, that in each particular valency grade an atom enters, it assumes quite new properties which are, in general, in no way connected with those it possessed in previous valency states.

For example the copper atom, when in the mono-valent state possesses properties very much akin to those possessed by the silver atom — producing for example, like Ag insoluble halide salts.

In the diad state, however, it produces compounds which seem in no way to resemble those of Ag.

The great Russian chemist, Mendelèef makes some interesting remarks regarding this point; he says (Principles 2, 416):

„Copper in its cuprous compounds is so analogous to silver, that were there no cupric compounds, or if silver gave stable compounds of the higher oxide AgO (corresponding to CuO) the resemblance would be as close as that between Cl and Br or Zn and Cd .

In the cupric state copper presents properties which make it resemble Zn , Fe'' , Ni'' &c. judging from the insolubility of the carbonates, phosphates and similar salts.“

This is not only the case with copper, but of almost every other element also, which can exist in several distinct valency grades.

In fact, in the words of Locke (Amer. Chem. Jr. (1898) 20. 581):

„The properties of the compounds of an element in two different degrees of oxidation differ absolutely from one another; and in the two, the element appears in two entirely different rôles.“

The cause of this is simple. The element when it changes its valence changes the attractive force which it exerts on other atoms, both relatively and absolutely, and this causes a change in its chemical properties, which are decided by these forces. For example in the case of Cu and Ag we have the following thermal data:

$$\begin{array}{ll} (\text{Cu}', \text{Cl}) = 32.9 = f_1' & (\text{Ag}, \text{Cl}) = 29.2 = f_1 \\ (\text{Cu}', \text{Br}) = 25.0 = f_2' & (\text{Ag}, \text{Br}) = 22.7 = f_2 \end{array}$$

whence:

$$\begin{array}{l} \frac{f_1'}{f_1} = \frac{32.9}{29.2} = 1.12 \\ \frac{f_2'}{f_2} = \frac{25.0}{23.0} = 1.10 \end{array}$$

That is to say, the attractive force which the Ag' atom exerts on Cl , Br , are proportional to the attractive forces which the Cu' atom exerts on the same radicles. And this is the reason

of the chemical similarity of mono-valent silver and mono-valent copper atoms, as will be explained in the next chapter.

In the case of cupric copper, Cu'' , however, the attractive forces are different and are proportional to those of Fe'' (ferrous iron) as the following thermal data shows:

$$\begin{array}{ll} (\text{Cu}''_{1/2}, \text{O}_{1/2}) = 18.58 = f_3' & (\text{Fe}''_{1/2}, \text{O}_{1/2}) = 32.3 = f_3 \\ (\text{Cu}''_{1/2}, \text{Cl}) = 25.81 = f_4' & (\text{Fe}''_{1/2}, \text{Cl}) = 41.0 = f_4 \\ (\text{Cu}''_{1/2}, \text{Se}_{1/2}) = 4.85 = f_5' & (\text{Fe}''_{1/2}, \text{Se}_{1/2}) = 9.22 = f_5 \end{array}$$

whence:

$$\frac{f_3'}{f_3} = \frac{18.6}{32.3} = 0.58$$

$$\frac{f_4'}{f_4} = \frac{25.81}{41.00} = 0.63$$

$$\frac{f_5'}{f_5} = \frac{4.85}{9.22} = 0.52$$

so that the cupric atom attracts other atoms with an intensity of force which is roughly proportional to that which ferrous iron exerts, but is only half as great.

And this is why the cupric atoms, present properties similar to those of the ferrous atoms, and different from those of the mono-valent silver atoms.

To find a mathematical expression from which can be deduced the characteristic surface of any given element.

Yet $\Phi, \Psi, X \dots$ be the characteristic surfaces as previously determined of the successive elements A, B, C, \dots whose atomic weights are $\alpha, \beta, \gamma \dots$. Now let a function ω be assumed such that

$$\omega = \alpha\Phi + \beta\Psi + \gamma X + \dots$$

Whence

$$\frac{d\omega}{d\alpha} = \Phi$$

$$\frac{d\omega}{d\beta} = \Psi$$

$$\frac{d\omega}{d\gamma} = X$$

&c. &c.

That is to say, by simply differentiating ω with respect to $\alpha, \beta, \gamma \dots$ we obtain the characteristic surfaces of the elements, which possess the atomic weights $\alpha, \beta, \gamma \dots$

Hence ω is the required mathematical expression.

ω is therefore a very remarkable function. In it is comprised the characteristic surface of every element, and therefore the properties of every element, which depend directly or indirectly upon the attractive forces it exerts.

ω therefore is an analytical expression which includes in a concise form the whole range of chemical facts relating to the elements and their properties — that is to say, practically the whole of inorganic chemistry as known to us. We have therefore theoretically solved the problem of replacing the whole of descriptive inorganic chemistry by a single mathematical expression consisting of 3 variables only, from which can be deduced, theoretically at least, the chemical properties of any given element and its compounds.

The normal affinity surface.

We will in the following chapters confine ourselves to the discussion of one particular affinity surface which is of special interest. At ordinary temperatures and pressures every element attains a condition of maximum chemical repose or equilibrium when in one particular valency grade.

For example, under ordinary circumstances iron comes to rest in the ferric grade of oxidation, higher grades and lower grades of combination being unstable.

If we imagine each of the elements of the Periodic System to assume its normal valence, and then measure the force which an element A (also in its normal valency grade) exerts on each of the other elements when in this normal valency condition, we would thus derive an affinity surface which we will call the "normal affinity surface" of A.

This surface is only one of the 8^{120} different affinity surfaces capable of being constructed for an element. But it is the only one, usually, for which there exists sufficient data to construct its approximate shape; and the results brought to light by the construction of these surfaces are sufficiently remarkable as will be seen later.

Before proceeding to construct this affinity surface for the various elements we will first discuss the causes which determine the chemical similarity of elements; and then later we will show how it follows from this that there is an essential connection between the form of the affinity surface of an element and its properties.

Empirical nature of the affinity surface.

A difficulty will probably occur to the reader. We cannot classify the elements with any degree of certainty, and so the "net-work" used in the previous investigation as base is of very uncertain value. A little consideration will show, however, that this difficulty is only an imaginary one. For it does not matter in the least how or in what order we arrange the elements, because their affinities do not change with the way they are arranged on a diagram. Their affinities are fixed constants, and it is a pure matter of personal convenience whether we choose to arrange the elements in a single long line, or in squares.

I arrange them according to the Periodic System simply for convenience. Any other conceivable arrangement will do equally well.

Of course, the form of the affinity surface would alter with every different way in which we arrange the elements. For instance, if we arrange them all in the order of their atomic weights along a straight line, the affinity surface would degenerate into a single wave curve thus:

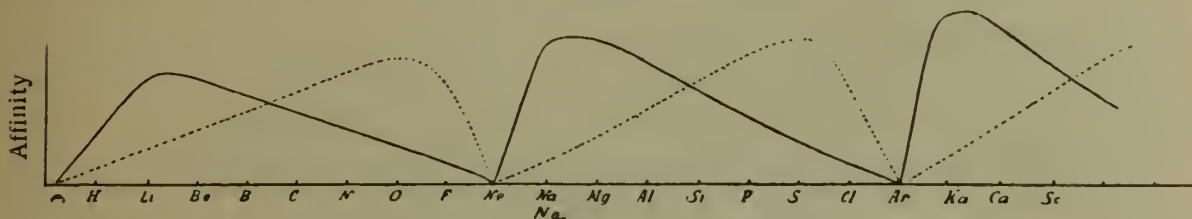


Fig. 2.

Shape of the curve of affinity for non-metal.

The dotted line gives the shape of the curve of affinity for a metal.

The only condition which must necessarily be fulfilled by the arrangement of the elements is that every known element should be capable of being represented in the scheme of the diagram, and that its position can be fixed by a number or numbers. We can then deduce from the equation of the affinity curve or surface by a process similar to that previously employed the attractive force exerted by the element whose affinity curve is given on a given element A, by simply substituting the numerical constant or constants which distinguish A in the equation of the curve.

Compounds can also be represented by surfaces.

It is not our intention to fully discuss this subject here, because we intend to discuss this and allied subjects in the second part of this essay.

We merely wish to point out that the methods employed for representing elements by means of characteristic surfaces can be extended to compounds as well.

In fact, the compounds of an element may, mathematically, be looked upon as the original element itself modified by the addition of other atoms.

For example, ammonia, NH_3 , may be looked upon as a nitrogen atom whose attractive power is modified by the addition of three hydrogen atoms, the whole forming a system having quite different properties to the original nitrogen atom.

The system of attractive forces $f_1, f_2, f_3, f_4 \dots f_n$, with which the original nitrogen atom attracted other atoms may be looked upon as still present in the nitrogen atom modified by three atoms of hydrogen — that is to say in ammonia.

This is clear because ammonia like nitrogen must also, in general, exert n different attractive forces on the n different elementary forms of matter. But the original forces in the nitrogen atom have become so altered and modified in intensity and relative magnitude by the influences of the hydrogen atoms as to pass into an entirely different set of forces $F_1, F_2, F_3 \dots F_n$ which are in no way comparable with the original system. If now we think of the compound NH_3 as replaced by these forces (as in the case of elements) then the operation of combining the N atom with 3 hydrogen atoms is algebraically equivalent to transforming the original system of forces $f_1, f_2, f_3 \dots f_n$ into a new system $F_1, F_2, F_3 \dots F_n$.

And if the original system of forces determine in the way previously indicated a surface which represents the properties of the original nitrogen, then the new system of forces $F_1, F_2, F_3, F_4 \dots F_n$ will determine a corresponding surface which represents the properties of nitrogen to which three hydrogen atoms are added on — that is, of ammonia.

So that geometrically considered, the effect of operating on the original nitrogen atom with three hydrogen atoms is to deflect the original surface into another surface, both of which are perfectly determinate when the magnitudes of $f_1, f_2, f_3 \dots f_n$ and $F_1, F_2, F_3 \dots F_n$ are known.

Hence the method pointed out in the previous pages of representing the properties of atoms by characteristic surfaces

determined by the affinities $f_1, f_2, f_3, f_4 \dots f_n$ of the atoms is applicable also the compounds formed by the union of these atoms.

This is otherwise obvious. For a molecule is a particle of matter composed out of a number of constituent atoms; and since each of the atoms in this molecule are replaceable by a system of forces, all these atomic forces must be compoundable together into a single set of forces which represents the external effect producible by the complete aggregate of atomic forces which go to compose the molecule — that is to say, which represent the external chemical effect producible by the complete molecule. Every molecule, therefore, must be in its turn replaceable by a single system of forces which will picture all the chemical effects the molecule is capable of producing.

Upon this basis it is possible to construct a theory of chemistry in which both elements and compounds are looked upon not as corporal material masses, but as separate systems of forces, each system being represented by a definite surface, — the operation of producing a compound from an element being thus followed by the change in the surface of the element when converted into the compound.

Thus chemistry can by means of Newton's Third Law of Motion be made to depend ultimately upon the analytical theory of surfaces, every chemical operation being represented by an analytical expression which represents quantitatively the transformation in properties brought about by that operation, without directly referring to the atoms and molecules as corporal material masses.



Chapter II.

The mechanical cause of the chemical similarity of elements and radicles.

Conditions which determine the chemical similarity of elements and radicles.

A casual survey of the elements reveals the fact that there exist some which exhibit a very great degree of chemical similarity to each other, and others which are widely unlike in properties.

Nevertheless the causes underlying the different behaviour of elements never seems to have been investigated in a general way. This we proceed to do in this chapter.

The chemical similarity of elements does not arise on account of equality in the weights of their atoms — for example Cl with an atomic weight of 35.5 is chemically similar to Br with an atomic weight of 80. Nor does it arise from equality of valence. For example, Boron is chemically similar to silicon, and yet the boron atom is trivalent and the silicon atom is tetravalent. Yet boron and silicon are strikingly chemically similar. Hydrogen and chlorine are both univalent and are quite unlike chemically.

There is, however, a simple condition which determines the similarity or dissimilarity of different atoms, as we proceed to show.

Suppose we have two different atomic species A and B, defined (§ 2) by the attractive forces $f_1, f_2, f_3 \dots f_n$, and $f_1', f_2', f_3' \dots f_n'$, respectively.

Then (Chap. I, § 2) A and B will be perfectly chemically similar, that is to say, will react in precisely the same way chemically, if:

$$f_1 = f_1', f_2 = f_2', f_3 = f_3' \dots \dots f_n = f_n'$$

that is, if:

$$\frac{f_1}{f_1'} = \frac{f_2}{f_2'} = \frac{f_3}{f_3'} = \dots \dots = \frac{f_n}{f_n'} = 1.$$

I had previously imagined, after examing the case of fluorine and oxygen (see Chem. News **89**, 49 [1904]), that the chemical similarity of different atoms depended solely upon a capacity for exerting chemical forces of the same intensity.

But this though sufficient is not necessary; for there exist chemically similar elements (such as Cl and Br) in which this condition is not satisfied.

The bromine atom for example, exerts chemical forces of a much feebler intensity than the chlorine atom, as appears from a study of the heats of formation of corresponding chlorides and bromides.

$$(P, Cl^5) = 105$$

$$(P, Br^5) = 83$$

To solve this problem I undertook an exhaustive study of the stability of the corresponding compounds of chemically similar and chemically unlike elements; with the result that I succeeded in discovering a single simple condition which is invariably fulfilled by chemically similar atoms, and never fulfilled by chemically unlike atoms; and which is presumably the direct mechanical cause of the chemical similarity or otherwise of different atomic species.

I found from an examination of corresponding chlorine and bromine compounds, that if chlorine produces a compound of a certain degree of stability, that bromine also produces the corresponding compound of a somewhat weaker degree of stability.

When a compound of chlorine is very stable the corresponding bromine compound is also very stable, but not quite so stable as the chlorine compound. And when a compound of chlorine

is unstable, the corresponding bromine compound is also unstable, and somewhat more unstable than the chlorine compound.

It seems in fact, that the force exerted by the bromine atom is always less than the force exerted by the chlorine atom on a given element or radicle but is always proportional to it.

And precisely the same relationship holds between the corresponding compounds of sodium and potassium, sulphur and selenium, zinc and cadmium, and in fact between the compounds of all pairs of elements which exhibit a very close degree of chemical similarity. The condition, in fact, which must exist between the affinities of two different atomic species or radicles A and B in order that they may be chemically similar is this:

The chemical attractions which A exerts on the various elementary atoms or radicles, must be either equal or proportional to the chemical attractions which B exerts on the same atoms or radicles.

If we denote the attractions which A exerts by $f_1, f_2, f_3 \dots f_n$; and those which B exerts by $f_1', f_2', f_3' \dots f_n'$; then the mathematical expression for the condition of chemical similarity is:

$$\frac{f_1}{f_1'} = \frac{f_2}{f_2'} = \frac{f_3}{f_3'} = \dots = \frac{f_n}{f_n'} = \text{constant } K \dots (2)$$

If $K = 1$, then $f_1 = f_1'; f_2 = f_2'; f_3 = f_3'$ &c. &c.; and the two elements exerts forces of the same intensity; and this is obviously the condition, that A and may be perfectly chemically similar, for in this case B can replace A in any reaction without altering the nature or direction of the reaction, which is determined by these chemical forces. (Chap. I).

The closer K approaches unity, the closer the elements approach each other in their chemical properties.

And the more K departs from unity, the more will the resemblance between the elements fade, although so long as (2) holds true, the elements will always exhibit a chemical resemblance to each other — the one merely possessing the same chemical properties as the other in a more highly intensified form.

In fact, when $K = n$, the one element possesses the same chemical properties as the other, but intensified n -fold.

For example for the system fluorine and chlorine, K has the value 1.7 as the following thermal data shows (see later):

$$\begin{array}{ll} (F, Si^{1/4}) = 67.3 = f_1 & (Cl, Si^{1/4}) = 39.4 = f_1' \\ (F, H) = 37.6 = f_2 & (Cl, H) = 22 = f_2' \end{array}$$

whence

$$\frac{f_1}{f_1'} = \frac{67.3}{39.4} = 1.71$$

$$\frac{f_2}{f_2'} = \frac{39.4}{22} = 1.70$$

or

$$\frac{f_1}{f_1'} = \frac{f_2}{f_2'} = 1.7$$

This means, that fluorine possesses the same chemical properties as chlorine, but intensified 1.7-fold.

The constant K , in fact, bears to two elements a relation similar to that which the ratios of their two eccentricities bear to two ellipses or hyperbolae.

And in this sense K may be said to measure the chemical similarity of two elements just as the ratios of the two eccentricities measures the similarity of the two curves — the ratio being unity when the curves are perfectly similar.

In general the relationship (2) is not satisfied by the affinities of any two elements A and B selected at random.

We find, however, that the more closely their affinities conform to this law the closer is their chemical resemblance.

And that the more widely their affinities depart from this law, the remoter is their chemical resemblance.

So that in the case of elements which behave in a quite different way chemically, this relationship is not even remotely satisfied as we will presently show.

No two elements are perfectly chemically similar. All exhibit certain chemical peculiarities which distinguish one from the other. Therefore the relation (2) is never exactly satisfied by

the affinities of two elements, but is merely the limiting condition which is more and more exactly fulfilled as the elements approach more and more exactly to perfect chemical similarity.

For atoms of the same element alone, is condition (2) exactly fulfilled, K here taking the value unity since the forces are now of the same intensity.

It may be noted, that many of the so-called radicles can play the part of elementary atoms, although quite incapable of existing separately (for example $-\text{NH}_4$, $-\text{CN}$) simply because they are arrangements of atoms so combined together as to exert forces of the same intensity as the elementary atoms of which they play the part.

The interpretation of these results as regards the form of the characteristic surface is very simple.

If the relation (1) is satisfied, then the characteristic surface of A and B absolutely coincide for $f_1, f_2, f_3, f_4 \dots f_n$ and $f_1', f_2', f_3', f_4' \dots f_n'$, the affinities of the two elements will coincide, each to each, and therefore their characteristic surfaces which depend upon these affinities must also coincide. And therefore the same arbitrary section of the corresponding arbitrary sections of the two characteristic surfaces will coincide.

More generally, if relation (2) alone is satisfied then the corresponding sections of the corresponding two characteristic surfaces will not in general coincide, but will take the form represented below (see fig. 2).

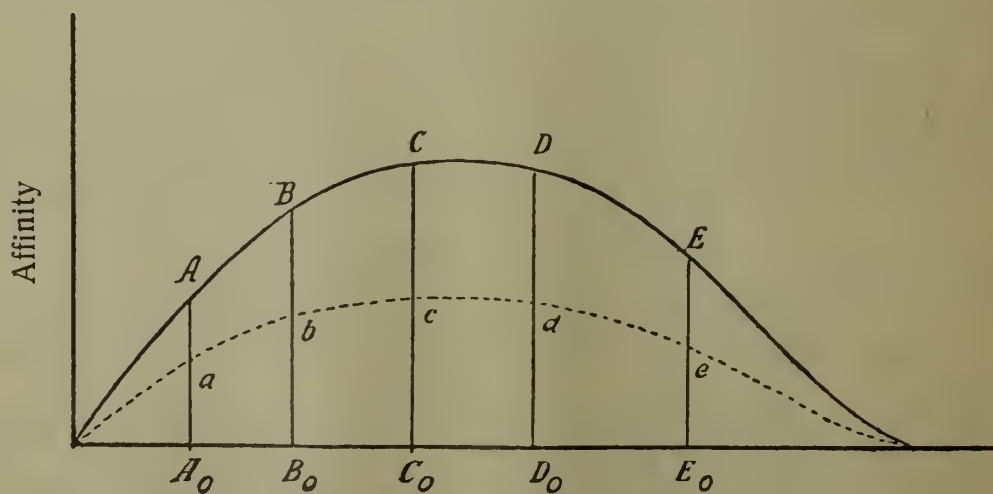


Fig. 3.

Let A, B, C, D, E , be any section of the characteristic surface of the first element A ; and let a, b, c, d, e , be the corresponding section of the B surface. Then the points A, B, C, D, E , are so related to the with respect to the corresponding points a, b, c, d, e , that

$$\frac{AA_0}{aA_0} = \frac{BB_0}{bB_0} = \frac{CC_0}{cC_0} = \dots = K$$

(in the particular case when $K = 1$, the curves A, B, C, D, E , coincides with a, b, c, d, e , as we have already pointed out). It will be noticed that so long as the relation (2) is obeyed no corresponding sections of the characteristic surfaces can intersect, i. e., the characteristic surface of the one element will lie wholly outside or wholly inside the characteristic surface of a chemically similar element, but can never lie partly outside and partly inside it.

In other words if $F(x, y, z) = 0$ be the equation of the characteristic surface of A , then $F(x, y, kz) = 0$ will be the characteristic surface of B . If however relation (2) is not satisfied, so that k is not a constant and the elements are not

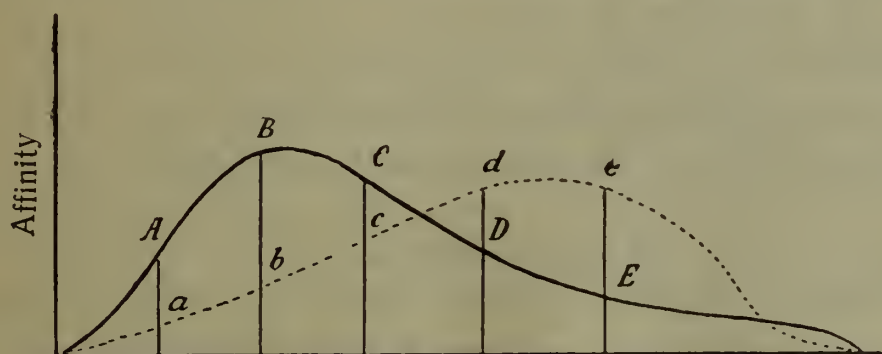


Fig. 4.

chemically similar, then in general any arbitrary section of the one characteristic surface of A will intersect in one or more points the corresponding section of the characteristic surface of B (see fig. 3). And the characteristic surface of A will lie partly outside and partly inside the characteristic surface of B . So that the equations of the characteristic surfaces have in this case quite

different forms, viz $F(x, y, z) = 0$ and $\Psi(x, y, z) = 0$ and cannot both be reduced to the same form by writing kz for z in the equation of the one.

It follows that:

The characteristic surfaces of chemically similar elements are of a similar shape, and those of dissimilar elements of a dissimilar shape.

We will now arrange the available data to show the general truth of the preceding generalisations. We will show:

1. That when we contrast chemically unlike elements such as hydrogen and chlorine, oxygen and iodine, that the relations

$$\frac{f_1}{f_1'} = \frac{f_2}{f_2'} = \frac{f_3}{f_3'} = \dots = \frac{f_n}{f_n'} = K$$

are not even distantly fulfilled.

2. That on the other hand when we contrast elements which in general betray a very close degree of resemblance, the above relationships are fulfilled.

The difficulty that we meet with here is to find numerical values for f_1 and f_1' , f_2 and f_2' f_n and f_n' — the corresponding forces which A and B exert on the other elements.

It is no difficult matter when studying the forces with which two elements A and B attract (say) chlorine atoms, to decide whether A or B attract Cl with the greatest force. A careful comparison of the chemical properties of the chlorides ACl and BCl — their temps^o of decomposition, the reagents which decompose them &c. &c., will reveal this. We can by this means find out whether one element attracts the chlorine very much more strongly or very much more weakly than the other. But to give precisely numerical values to f_r and f_r' is the difficulty.

To do this we are forced to fall back upon thermal data, and take the heat which is evolved in the formation of a compound as measuring the attracting forces urging the atoms together. At the absolute zero this might be the case; but at ordinary temperatures it will differ from that more or less.

And a further error is introduced by the fact that the heat of formation usually given are not the true heats of formation of compounds — namely, the heat evolved, when the free atoms of the constituent elements combine together to produce the compounds — but are merely difference effects which may be zero or negative, whereas the true heats of formation must always be positive. Cases undoubtedly exist where of two compounds, that which is the most unstable has the greatest H.F.

To give one example, SiH_4 has a greater H.F. than CH_4

$$[\text{Si}^{1/4}, \text{H}] = 8.2 \qquad [\text{C}^{1/4}, \text{H}] = 5.2$$

Yet undoubtedly of these two bodies the H is attracted to the C in CH_4 with a greater intensity than it is attracted to the Si in SiH_4 . The whole chemical behaviour of the two compounds is how that is the case. For example, while CH_4 is unaffected at a red heat, SiH_4 under the same conditions is completely decomposed into its constituents.

It is only when the heat evolved in the formation of a compound, is very great, that it can be taken as measuring approximately the attractive forces, for in this case the incidental errors become small in comparison with the heat evolved. When the H.F. is small the incidental errors may become large enough to give the unstabler compound the greater H.F. as in the case just mentioned.

1. To show, that when we contrast chemically unlike elements the relations

$$\frac{f_1}{f_1'} = \frac{f_2}{f_2'} = \frac{f_3}{f_3'} = \dots = \frac{f_n}{f_n'} = K$$

are not even remotely satisfied, but that K varies widely and irregularly for every different ratio.

As typical pairs of unlike elements, we will contrast H with Cl, on the one hand, O with I on the other. In neither case are the relations satisfied.

Hydrogen and Chlorine.

$[H, Li] = 21.6 = f_1'$	$[Cl, Li] = 94 = f_1$
$[H, Na] = 12 = f_2'$	$[Cl, Na] = 98 = f_2$
$[H, C^{1/4}] = 5.4 = f_3'$	$[Cl, C^{1/4}] = 13.5 = f_3$
$[H, Si^{1/4}] = 8.2 = f_4'$	$[Cl, Si^{1/4}] = 39 = f_4$
$[H, N^{1/3}] = 4.0 = f_5'$	$[Cl, N^{1/3}] = -13 = f_5$
$[H, P^{1/3}] = 3.86 = f_6'$	$[Cl, P^{1/3}] = 25 = f_5$
$[H, As^{1/3}] = -12.2 = f_7'$	$[Cl, As^{1/3}] = 24 = f_7$
$[H, Sb^{1/3}] = -28.1 = f_8'$	$[Cl, Sb^{1/3}] = 30.46 = f_8$
$[H, O^{1/2}] = 34.2 = f_9'$	$[Cl, O^{1/2}] = -9 = f_9$
$[H, S^{1/4}] = 2.3 = f_{10}'$	$[Cl, S^{1/4}] = 6 = f_{10}$

Whence

$$\frac{f_1}{f_1'} = \frac{94}{21.6} = 4.3$$

$$\frac{f_6}{f_6'} = \frac{25}{3.86} = 6.5$$

$$\frac{f_2}{f_2'} = \frac{98}{13} = 7.3$$

$$\frac{f_7}{f_7'} = \frac{24}{-12.2} = -1.9$$

$$\frac{f_3}{f_3'} = \frac{13.5}{54} = 2.3$$

$$\frac{f_8}{f_8'} = \frac{30.46}{-28.1} = -1$$

$$\frac{f_4}{f_4'} = \frac{39}{8.2} = 4.7$$

$$\frac{f_9}{f_9'} = \frac{-9}{34.2} = -0.26$$

$$\frac{f_5}{f_5'} = \frac{-13}{4.0} = -3.2$$

$$\frac{f_{10}}{f_{10}'} = \frac{6}{2.3} = 2.6$$

Hence K takes in succession each of the following values: 4.3, 7.5, 2.3, 4.7, -3.2, 5.5, -1.9, -1, -0.26, 2.6.

The ratio is in no case constant but varies widely and irregularly. The varying of K would be very much greater if we only knew the H.F. of all the corresponding compounds; but as a matter of fact experimental difficulties limit the determination of the H.F. of compounds only to those which are stable enough to exist at an ordinary temperature. Many compounds of chlorine are known of great stability, whereas the corresponding hydrides are too unstable to exist at ordinary temperatures eg. $PbCl_2$ and PbH_2 .

Iodine and Oxygen.

(H, I) = -6 = f_1'	(H, $O^{1/2}$) = 34.2 = f_1
(I, Cu) = 17.6 = f_2'	($O^{1/2}$, $Cu^{1/2}$) = 18.6 = f_2
(I, Ag) = 14 = f_3'	($O^{1/2}$, Ag) = 3 = f_3
(I, Li) = 64 = f_4'	($O^{1/2}$, Li) = 70.6 = f_4
(I, $Mg^{1/2}$) = 42.4 = f_5'	($O^{1/2}$, $Mg^{1/2}$) = 70.0 = f_5
(I, Na) = 69 = f_6'	($O^{1/2}$, Na) = 45.5 = f_6
(I, $Hg^{1/2}$) = 11.1 = f_7'	($O^{1/2}$, $Hg^{1/2}$) = 11.0 = f_7
(I, K) = 80.1 = f_8'	($O^{1/2}$, K) = 47.4 = f_8
(I, $Ca^{1/2}$) = 53.6 = f_9'	($O^{1/2}$, $Ca^{1/2}$) = 72.4 = f_9
(I, $Sr^{1/2}$) = 71.7 = f_{10}'	($O^{1/2}$, $Sr^{1/2}$) = 64.2 = f_{10}
(I, Cl) = 2.1 = f_{11}'	($O^{1/2}$, Cl) = -9 = f_{11}
(I, S) = 5.0 = f_{12}'	($O^{1/2}$, $S^{1/4}$) = 17.7 = f_{12}
(I, $As^{1/3}$) = 9.5 = f_{13}'	($O^{1/2}$, $As^{1/3}$) = 25.77 = f_{13}
(I, $Si^{1/4}$) = 14.5 = f_{14}'	($O^{1/2}$, $Si^{1/4}$) = 54.8 = f_{14}
(I, $Pb^{1/2}$) = 22.1 = f_{15}'	($O^{1/2}$, $Pb^{1/2}$) = 25.1 = f_{15}

Whence

$$\frac{f_1}{f_1'} = \frac{34.2}{-6} = -5.7$$

$$\frac{f_8}{f_8'} = \frac{47.4}{80.1} = 0.59$$

$$\frac{f_2}{f_2'} = \frac{18.6}{17.6} = 1.06$$

$$\frac{f_9}{f_9'} = \frac{72.2}{53.6} = 1.35$$

$$\frac{f_3}{f_3'} = \frac{3}{14} = 0.21$$

$$\frac{f_{10}}{f_{10}'} = \frac{64.2}{71.7} = 0.89$$

$$\frac{f_4}{f_4'} = \frac{70.6}{64} = 1.10$$

$$\frac{f_{11}}{f_{11}'} = \frac{-9}{2.1} = -4.3$$

$$\frac{f_5}{f_5'} = \frac{70.0}{42.4} = 1.65$$

$$\frac{f_{12}}{f_{12}'} = \frac{17.7}{5.0} = 3.54$$

$$\frac{f_6}{f_6'} = \frac{45.5}{69} = 0.66$$

$$\frac{f_{13}}{f_{13}'} = \frac{25.77}{9.6} = 2.7$$

$$\frac{f_7}{f_7'} = \frac{11}{11.1} = 0.99$$

$$\frac{f_{14}}{f_{14}'} = \frac{54.8}{14.5} = 3.78$$

$$\frac{f_{15}}{f_{15}'} = \frac{25.1}{22.1} = 1.14$$

K, therefore, takes any of the following values: —5.7, 1.06, 0.21, 1.10, 1.65, 0.66, 0.99, 0.59, 1.35, 0.89, —4.3, 3.54, 2.7, 3.78, 1.14, and hence is not even remotely constant.

An examination of the corresponding compounds of any two dissimilar elements will reveal the same peculiarity.

2. Chemically similar elements.

When however we contrast chemically similar elements, a very different relationship is observed. K remains approximately constant.

Chlorine and Bromine.

(Cl, Cu) = 32.9 = f_1	(Br, Cu) = 25 = f_1'
(Cl, Ag) = 29.2 = f_2	(Br, Ag) = 22.7 = f_2'
(Cl, Li) = 93.8 = f_3	(Br, Li) = 80 = f_3'
(Cl, Na) = 97.7 = f_4	(Br, Na) = 85.8 = f_4'
(Cl, K) = 105.6 = f_5	(Br, K) = 95.3 = f_5'
(Cl, $\text{Ca}^{1/2}$) = 84.6 = f_6	(Br, $\text{Ca}^{1/2}$) = 70.4 = f_6'
(Cl, $\text{Sr}^{1/2}$) = 92.3 = f_7	(Br, $\text{Sr}^{1/2}$) = 78.8 = f_7'
(Cl, $\text{Ba}^{1/2}$) = 97.3 = f_8	(Br, $\text{Ba}^{1/2}$) = 85.0 = f_8'
(Cl, $\text{Zn}^{1/2}$) = 48.6 = f_9	(Br, $\text{Zn}^{1/2}$) = 40.0 = f_9'
(Cl, $\text{Hg}^{1/2}$) = 27.2 = f_{10}	(Br, $\text{Hg}^{1/2}$) = 20.3 = f_{10}'
(Hg, Cl) = 32.6 = f_{11}	(Br, Hg) = 24.5 = f_{11}'
(Cl, $\text{Al}^{1/3}$) = 53.66 = f_{12}	(Br, $\text{Al}^{1/3}$) = 41.0 = f_{12}'
(Cl, $\text{As}^{1/3}$) = 23.8 = f_{13}	(Br, $\text{As}^{1/3}$) = 19.7 = f_{13}'
(Cl, $\text{Sb}^{1/3}$) = 30.46 = f_{14}	(Br, $\text{Sb}^{1/3}$) = 25.63 = f_{14}'
(Cl, $\text{Pb}^{1/2}$) = 41.0 = f_{15}	(Br, $\text{Pb}^{1/2}$) = 36.0 = f_{15}'

Whence

$$\frac{f_1}{f_1'} = \frac{32.9}{25} = 1.32$$

$$\frac{f_5}{f_5'} = \frac{105.6}{95.3} = 1.11$$

$$\frac{f_2}{f_2'} = \frac{29.2}{22.7} = 1.29$$

$$\frac{f_6}{f_6'} = \frac{84.6}{70.4} = 1.20$$

$$\frac{f_3}{f_3'} = \frac{93.8}{80} = 1.17$$

$$\frac{f_7}{f_7'} = \frac{92.3}{78.8} = 1.18$$

$$\frac{f_4}{f_4'} = \frac{97.7}{85.8} = 1.14$$

$$\frac{f_8}{f_8'} = \frac{97.3}{85.0} = 1.15$$

$$\frac{f_9}{f_9'} = \frac{48.6}{40.0} = 1.21 \qquad \frac{f_{12}}{f_{12}'} = \frac{53.66}{71.0} = 1.30$$

$$\frac{f_{10}}{f_{10}'} = \frac{27.2}{20.3} = 1.34 \qquad \frac{f_{13}}{f_{13}'} = \frac{23.8}{19.7} = 1.21$$

$$\frac{f_{11}}{f_{11}'} = \frac{32.6}{24.5} = 1.33 \qquad \frac{f_{14}}{f_{14}'} = \frac{30.46}{25.63} = 1.19$$

$$\frac{f_{15}}{f_{15}'} = \frac{41}{36} = 1.14$$

K is here throughout the series approximately constant, never becoming greater than 1.34 nor less than 1.11.

When we contrast these values of K with the previous values, we see how closely constant K remains. The values of K range in the case of H and Cl from 7.5 to — 3.2 and in the case of O and I, from — 5.7 to 3.78.

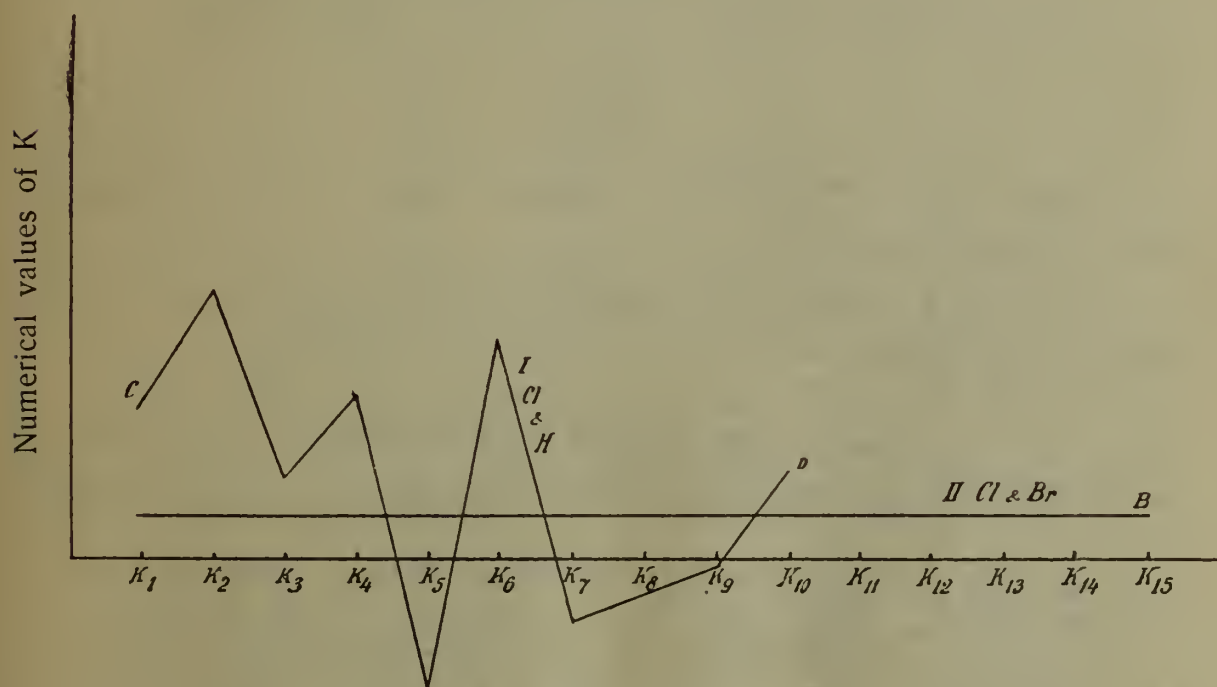


Fig. 5.

Showing the approximate constancy of K for similar elements (Cl and Br) and its variation for dissimilar elements (Cl and H).

The erratic line CD records the successive values of K for the system Cl and H. The nearly straight line AB records the successive values of K for the system Cl and Br.

The approximate constancy of K for similar elements, and its variation for dissimilar elements is best demonstrated graphically. Writing K_1 for $\frac{f_1}{f_1'}$; K_2 for $\frac{f_2}{f_2'}$; K_n for $\frac{f_n}{f_n'}$; and taking $K_1, K_2, K_3, K_4 \dots K_n$ as abscissae, and the successive numerical values as ordinates, we find for the system Cl and H an erratic line, for the system Cl and Br an almost straight line parallel to the axis of x (fig. 5).

Fluorine and Chlorine.

The only data available is the following:

$$\begin{array}{ll} (\text{F, Si}^{1/4}) = 67.3 = f_1 & (\text{Cl, Si}^{1/4}) = 39.4 = f_1' \\ (\text{F, H}) = 37.6 = f_2 & (\text{Cl, H}) = 22 = f_2' \end{array}$$

Whence:

$$\frac{f_1}{f_1'} = \frac{67.3}{39.4} = 1.71$$

$$\frac{f_2}{f_2'} = \frac{37.6}{22} = 1.70$$

The ratio is therefore constant even for such different elements as H and Si.

The large value of K shows, that F possesses the same chemical properties as Cl, but intensified 1.70 times.

Sodium and Potassium.

The only data available is the following:

$$\begin{array}{ll} (\text{K, Cl}) = 105.6 = f_1 & (\text{Na, Cl}) = 97.7 = f_1' \\ (\text{K, Br}) = 95.3 = f_2 & (\text{Na, Br}) = 85.8 = f_2' \\ (\text{K, I}) = 80.1 = f_3 & (\text{Na, I}) = 69.1 = f_3' \\ (\text{K, O}^{1/2}) = 47.4 = f_4 & (\text{Na, O}^{1/2}) = 45.5 = f_4' \\ (\text{K, NH}_3) = 6.3 = f_5 & (\text{Na, NH}_3) = 5.2 = f_5' \end{array}$$

Whence:

$$\frac{f_1}{f_1'} = \frac{105.6}{97.7} = 1.08$$

$$\frac{f_2}{f_2'} = \frac{105.6}{97.7} = 1.08$$

$$\frac{f_3}{f_3'} = \frac{95.3}{85.8} = 1.11$$

$$\frac{f_4}{f_4'} = \frac{47.4}{45.5} = 1.05$$

$$\frac{f_5}{f_5'} = \frac{6.3}{5.2} = 1.21$$

It will be seen, that here also K is constant and very nearly equal to unity — a fact, which explains the great chemical resemblance of Na and K.

Potassium and Cäsium.

The only available data is the following:

$$\begin{array}{ll} (K, Br) = 95.3 = f_1' & (Cs, Br) = 99.8 = f_1 \\ (K, I) = 80.1 = f_2' & (Cs, I) = 86.6 = f_2 \end{array}$$

Whence:

$$\frac{f_1}{f_1'} = \frac{99.8}{95.3} = 1.05$$

$$\frac{f_2}{f_2'} = \frac{86.6}{80.1} = 1.08$$

Here again, K is constant and very nearly equal to unity. In the case of all the alkali metals this is so, and this is the reason why there exists such a close resemblance between them.

Zinc and Cadmium.

The only data available is the following:

$$\begin{array}{ll} (Zn, Cl_2) = 97.2 = f_1 & (Cd, Cl_2) = 93.0 = f_1' \\ (Zn, O) = 85.4 = f_2 & (Cd, O) = 75.5 = f_2' \end{array}$$

Whence:

$$\frac{f_1}{f_1'} = \frac{97.2}{93} = 1.04$$

$$\frac{f_2}{f_2'} = \frac{85.4}{75.4} = 1.13$$

Here again K is constant and nearly equal to unity, which accounts for the close resemblance of Zn and Cd.

Boron and Silicon.

The case is of great interest, in as much as B and Si possess a great degree of chemical similarity, and yet B is trivalent and Si tetravalent. The chemical similarity of elements does not, in fact, depend upon their valence but solely upon their attractive forces.

The following data — the only available — shows, that K is nearly equal to unity, a fact which explains the remarkable chemical resemblance of these two elements.

$$\begin{array}{ll} (B^{1/3}, Cl) = 34.70 = f_1' & (Si^{1/4}, Cl) = 39.4 = f_1 \\ (B^{1/3}, O^{1/2}) = 52.8 = f_2' & (Si^{1/4}, O^{1/2}) = 54.8 = f_2 \end{array}$$

Hence:

$$\begin{array}{l} \frac{f_1}{f_1'} = \frac{39.4}{34.7} = 1.13 \\ \frac{f_2}{f_2'} = \frac{54.8}{52.8} = 1.04 \end{array}$$

Calcium and Strontium.

$$\begin{array}{ll} (Ca^{1/2}, Cl) = 84.6 = f_1' & (Sr^{1/2}, Cl) = 92.3 = f_1 \\ (Ca^{1/2}, Br) = 70.4 = f_2' & (Sr^{1/2}, Br) = 78.8 = f_2 \\ (Ca^{1/2}, I) = 53.6 = f_3' & (Sr^{1/2}, I) = 71.7 = f_3 \\ (Ca^{1/2}, O^{1/2}) = 65.5 = f_4' & (Sr^{1/2}, O^{1/2}) = 64.2 = f_4 \\ {}^{1/4}(Ca, O^2) = 37.6 = f_5' & {}^{1/4}(Sr, O^2) = 35.5 = f_5 \end{array}$$

Whence:

$$\begin{array}{l} \frac{f_1}{f_1'} = \frac{92.3}{84.6} = 1.09 \\ \frac{f_2}{f_2'} = \frac{78.8}{70.4} = 1.12 \end{array}$$

$$\frac{f_3}{f_3'} = \frac{71.7}{53.6} = 1.33$$

$$\frac{f_4}{f_4'} = \frac{64.2}{65.5} = 0.98$$

$$\frac{f_5}{f_5'} = \frac{35.5}{37.6} = 0.94$$

Here again K is nearly equal to unity, a fact which explains the chemical resemblance of Ca and Sr.

Strontium and Barium.

$(\text{Sr}^{1/2}, \text{Cl}) = 92.3 = f_1'$	$(\text{Ba}^{1/2}, \text{Cl}) = 97.3 = f_1$
$(\text{Sr}^{1/2}, \text{Br}) = 87.8 = f_2'$	$(\text{Ba}^{1/2}, \text{Br}) = 85.0 = f_2$
$(\text{Sr}^{1/2}, \text{I}) = 71.7 = f_3'$	$(\text{Ba}^{1/2}, \text{I}) = 72.3 = f_3$
$(\text{Sr}^{1/2}, \text{O}^{1/2}) = 64.2 = f_4'$	$(\text{Ba}^{1/2}, \text{O}^{1/2}) = 62.1 = f_4$
$^{1/4}(\text{Sr}, \text{O}^2) = 35.5 = f_5'$	$^{1/4}(\text{Ba}, \text{O}^2) = 34.0 = f_5$

Whence:

$$\frac{f_1}{f_1'} = \frac{97.3}{92.3} = 1.05$$

$$\frac{f_2}{f_2'} = \frac{85.0}{78.8} = 1.08$$

$$\frac{f_3}{f_3'} = \frac{72.3}{71.7} = 1.01$$

$$\frac{f_4}{f_4'} = \frac{62.1}{64.2} = 0.97$$

$$\frac{f_5}{f_5'} = \frac{34.0}{35.5} = 0.96$$

Here again K is nearly equal to unity, which accounts for the great chemical similarity of Sr and Ba.

Nickel and Cobalt.

The only available data is the following:

$$(\text{Ni}^{1/2}, \text{Cl}) = 37.2 = f_1' \qquad (\text{Co}^{1/2}, \text{Cl}) = 38.2 = f_1$$

4*

$$\begin{array}{ll}
 (\text{Ni}^{1/2}, \text{Se}^{1/2}) = 9.21 = f_2' & (\text{Co}^{1/2}, \text{Se}^{1/2}) = 9.64 = f_2 \\
 (\text{Ni}^{1/2}, \text{Te}^{1/2}) = 7.55 = f_3' & (\text{Co}^{1/2}, \text{Te}^{1/2}) = 7.65 = f_3
 \end{array}$$

Whence:

$$\frac{f_1}{f_1'} = \frac{38.2}{37.2} = 1.02$$

$$\frac{f_2}{f_2'} = \frac{9.64}{9.21} = 1.05$$

$$\frac{f_3}{f_3'} = \frac{7.65}{7.55} = 1.01$$

Here again K is constant and very nearly equal to unity, as we should expect from the remarkable chemical resemblance of Co to Ni.

Antimony and Bismuth.

The data available is meagre:

$$\begin{array}{ll}
 (\text{Sb}^{1/3}, \text{Cl}) = 30.46 = f_1 & (\text{Bi}^{1/3}, \text{Bi}) = 30.21 = f_1' \\
 (\text{Sb}^2, \text{O}^3, 3\text{H}_2\text{O}) = 167.52 = f_2 & (\text{Bi}^2, \text{O}^3, 3\text{H}_2\text{O}) = 137.74 = f_2'
 \end{array}$$

Whence:

$$\frac{f_1}{f_1'} = \frac{30.46}{30.21} = 1.01$$

$$\frac{f_2}{f_2'} = \frac{167.4}{137.4} = 1.21$$

The preceding pages contain practically all the available thermal data for comparing the corresponding compounds of chemically similar elements. In every case where elements possess a great degree of similarity, K is approximately constant, and very often nearly unity. And in every case where elements differ widely in their chemical properties, precisely the reverse holds true.



Section 2.

Theory of chemically similar compounds.

We have examined the conditions which determine the chemical similarity of single atoms or radicles.

We now proceed to the case of chemically similar compounds. It does not strike one at first as remarkable that two entirely different chlorides such as BCl_3 and SiCl_4 should be chemically similar. The fact is so familiar, that one hardly stops to consider why this should be the case. Yet there is a definite mechanical reason why some compounds resemble each other chemically closely, and why others differ entirely in properties .-eg. why on the one hand SiO_2 resembles B_2O_3 and why on the other KCl differs in every respect from ICl .

We proceed in this section to consider the mechanical causes on which depend the chemical similarity or otherwise of different compounds.

Chemically similar compounds.

If two compounds produce similar chemical effects under similar conditions we say the bodies are chemically similar. For example NaOH and KOH are chemically similar substances, because any reaction which the one compound brings about under a given set of conditions, will also in general be brought about by the other under the same conditions. So that we can replace the one by the other without causing any marked change in the nature of the reaction.

A little consideration will show that chemically similar substances, must react to produce chemically similar substances, for

example, NaOH and KOH react with HCl to produce NaCl and KCl respectively, which in their turn are chemically similar.

Maximum attainable degree of chemical similarity.

Suppose a quantity of any homogeneous compound be divided into two equal portions A and B, and then each sealed up separately into a different packet.

If we were unaware of the identity of the material composing the two packets, we might erroneously regard each as containing a different chemical compound.

If we then proceed to separately investigate the chemical properties of the two supposed compounds, we would speedily come to the conclusion that we were dealing with two remarkably similar bodies, inasmuch as we would find that any chemical reaction which under a given set of conditions can be produced by A, can also under the same conditions be produced by B.

The two compounds, in fact, would be perfectly similar in all respects. Such a degree of similarity is the maximum which can be attained by any two chemical compounds. The degree of divergence from this standard enables us to judge of the degree of resemblance which exists between two different substances.

Conditions which determine the chemical similarity of compounds.

We will first deal with the simplest case of binary compounds suppose there exists two elementary atoms A and B, and that they each combine with the same third atom C to produce respectively the compounds AC and BC.

The conditions which must be fulfilled by the atoms A and B in order that each of the two compounds AC and BC may be chemically similar — i.e. react in the same way towards reagents — is this:

Both the atoms A and B must in general attract the same atoms or radicles with nearly the same (more strictly, with pro-

portional) intensity of force — that is, A and B must be chemically similar.

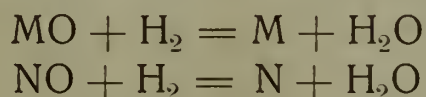
For when this condition is fulfilled C is attached to A and to B with nearly the same intensity of force; and consequently any influence which is capable of removing C the one atom, will be capable of removing C from the other and thus bring about a chemical change in both compounds. Moreover the chemical change will be a similar one in both cases; for since each of the atoms A and B exercise the same attractive power on the same atoms or group of atoms, it follows that when in the compound AC, the C is by a given operation replaced by another atom or atomic group X so as to produce the compound AX, then necessarily also in the compound BC, the C will also be removed by this same operation, and in its place will be substituted the same group X, which will be held both by A and by B with the same intensity of attractive force.

And thus the two compounds AC and BC will always react in the same way. For a similar reason so will AX and BX.

Let us illustrate this by the metallic oxides.

Suppose we have two metallic atoms M and N combined with oxygen to form, say, MO and NO.

Now if we act on each of each of these oxides with H gas, in general the H will at some temperature or other tear away the O from the metallic atom and leave it in the free state :



The temperature at which this occurs, however, may differ widely in the two cases.

For example if M attracts the Oxygen very much more intensely than does N, then in general a very much higher temperature will be required to reduce MO than to reduce NO. For example, Na_2O is much harder to reduce than Ag_2O ; Fe_2O_3 than Au_2O_3 . The two oxides, therefore, will present quite different chemical properties, if both are viewed under the same conditions of temperature and pressure the one reacting with reagents which leave the other unaffected, and vice-versa.

But if the oxygen is attached with the same force to each metal, then in general, the same temperature will suffice to bring about reduction. The oxides will thus present a very similar chemical behaviour, each parting with O with the same degree of readiness or difficulty.

It is for this reason that the oxides of the noble metals -e.g.- Pt_2O , Ag_2O , Au_2O_3 , &c. appear to us so similar, because they are all reduced to metal under the same conditions, -all holding O with about the same feeble force.

We have chosen the case of the metallic oxides to illustrate the fact that if C should be attached to both A and B with the same intensity of force, then in general the same influence which will remove C from A will also remove C from B, and thus in this respect the two compounds AC and BC will react similarly.

But, the condition that A and B should attract the same radicles generally, and not only C alone, with the same intensity of force, is a condition no less important in determining the chemical similarity of the two compounds.

For example in the above case the metals M and N are only left free because in general each possesses the similar property of attracting hydrogen only with a feeble intensity, and so do not combine with it:



If this was not the case the above reaction would take a quite different form. For example suppose it happened that the O was attached both to M and to N with the same force, and yet M in addition possessed a very intense attraction for H whereas N did not. Then in both cases the H would separate the O from M and N; but whereas in the one case it would leave N free, in the other case it would combine with M, and thus the two actions would in our eyes appear quite dissimilar; thus:



For example, in Cl_2O and Pd_2O the O is bound both to the Cl and to the Pd with intensities of force so nearly equal to that hydrogen is capable of removing the O from both sets of molecules under the same conditions.

Yet the two reactions take to our eyes a very different course because Cl happens to have an intense attraction for H, whereas Pd has not; so that the Pd is left free, whereas the Cl appears firmly combined with the H as a volatile gas:



More generally if instead of treating the metallic oxides with molecules of hydrogen, we treated them with other kinds of molecules which combine in addition with M and N, a chemical similarity will only appear if M and N posses the capacity of combining with the same radicles with nearly the same intensity of force; for example:



If M attracted Cl strongly and N did not, the reaction would take to our eyes very different forms, and the two oxides MO and NO would not appear chemically similar. It is not necessary to lay any restrictions upon the number of atoms contained in the two compounds; nor must the number of atoms in each compound be equal; for example MO_3 and WO_3 are chemically similar and both contain 4 atoms; BCl_3 and SiCl_4 are chemically similar and one contains 4 atoms and the other 5. WO_3 and Fe_2O_3 are chemically similar, and one contains 4 and the other 5 atoms.

If instead of C being identical in both compounds, we suppose its place is taken by two different atoms C' and C'' , then an extension of the above reasoning will show that before the two compounds AC' and BC'' will react chemically in the same way, the following conditions must be fulfilled:

- I. Both A and B must attract the same radicles with the same intensity of force.*)
- II. Both C' and C'' must attract the same radicles with the same intensity of force.

In other words, of the 4 atoms A, B, C', C''; A and B must be chemically similar, and so also must C' and C''.

Chemically similar compounds have usually nearly the same heat of formation.

Suppose we form a compound by allowing its constituent atoms to combine together.

Then the heat evolved may be regarded as the true heat of formation of the compound.

At the absolute zero to temperature the heat thus evolved probably measures the force driving together the atoms and thus is a measure of the attractive force, force holding together the atoms in the molecule.

At temperatures above the absolute zero this is not the case; the heat then evolved does not measure the driving force, but is some function of it.

But we have seen by the preceeding theory that corresponding compounds which react in the same way are such as have the atoms attracted together in the molecule with nearly the same intensity of force; and that the closer the degree of chemical similarity the more nearly equal is this force. We should therefore expect that chemically similar compounds should have nearly the same heat of formation. As the true heats of formation of compounds are unknown, we are forced to fall back on their apparent heats of formation.

We give this for a number of compounds which are remarkable on account of their resemblance to each other.

It will be seen that the values of the H.F. correspond closely to the degree of chemical similarity manifested by the compounds, those compounds which resemble each other most

*) More strictly, with proportional intensities of force,

closely in the way they react being in general those which approach each other most closely as regards their heats of formation.

The theory is incomplete, inasmuch as we have not yet considered the case where the intensities of the attractive forces are proportional, not equal. The theory may be readily completed from the fact already proved, that chemically similar compounds must consist of chemically similar atoms or groups of atoms.

Chemically similar compounds to be contrasted.	Equivalent heats of formation.		
$\begin{cases} \text{B}_2\text{O}_3 \text{ and } \text{SiO}_2 \\ \text{BCl}_3 \text{ and } \text{SiCl}_4 \end{cases}$	$(\text{B}^{1/3}, \text{O}^{1/2}) = 52.8$ $(\text{B}^{1/3}, \text{Cl}) = 34.66$	$(\text{Si}^{1/4}, \text{O}^{1/2}) = 52.9$ $(\text{Si}^{1/4}, \text{Cl}) = 39.41$	
$\begin{cases} \text{NiCl}_2 \text{ and } \text{CoCl}_2 \\ \text{NiBr}_2 \text{ and } \text{CoBr}_2 \\ \text{NiO} \text{ and } \text{CoO} \end{cases}$	$\text{Ni} + \text{Cl}_2 + \text{Aq} = 95$ $\text{Ni} + \text{Br}_2 + \text{Aq} = 73$ $\text{Ni} + \text{O} + \text{Aq} = 63$	$\text{Co} + \text{Cl}_2 + \text{Aq} = 94$ $\text{Co} + \text{Br}_2 + \text{Aq} = 72$ $\text{Co} + \text{O} + \text{Aq} = 61$	
$\begin{cases} \text{ZnCl}_2 \text{ and } \text{CdCl}_2 \\ \text{ZnO} \text{ and } \text{CdO} \end{cases}$	$(\text{Zn}^{1/2}, \text{Cl}) = 24.3$ $(\text{Zn}^{1/2}, \text{O}^{1/2}) = 21.36$	$(\text{Cd}^{1/2}, \text{Cl}) = 23.3$ $(\text{Cd}^{1/2}, \text{O}^{1/2}) = 18.9$	
$\begin{cases} \text{CuCl} \text{ and } \text{AgCl} \\ \text{CuBr} \text{ and } \text{AgBr} \\ \text{CuI} \text{ and } \text{AgI} \end{cases}$	$(\text{Cu}, \text{Cl}) = 32.87$ $(\text{Cu}, \text{Br}) = 24.98$ $(\text{Cu}, \text{I}) = 17.60$	$(\text{Ag}, \text{Cl}) = 29.2$ $(\text{Ag}, \text{Br}) = 22.7$ $(\text{Ag}, \text{I}) = 14.0$	
$\begin{cases} \text{CaO}, \text{SrO}, \text{BaO} \\ \text{CaO}_2, \text{SrO}_2, \text{BaO}_2 \end{cases}$	$\frac{1}{2}(\text{Ca}, \text{O}) = 65.5$ $\frac{1}{4}(\text{Ca}, \text{O}^2) = 37.6$	$\frac{1}{2}(\text{Sr}, \text{O}) = 64.2$ $\frac{1}{4}(\text{Sr}, \text{O}^2) = 35.5$	$\frac{1}{2}(\text{BaO},) = 62.1$ $\frac{1}{4}(\text{Ba}, \text{O}^2) = 34.0$
$\begin{cases} \text{FeCl}_2 \text{ and } \text{CoCl}_2 \\ \text{FeBr}_2 \text{ and } \text{CoBr}_2 \\ \text{FeO} \text{ and } \text{CoO} \\ \text{Fe}(\text{SO}_4 \text{ a. } \text{Co}(\text{SO}_4)) \end{cases}$	$\text{Fe} + \text{Cl}_2 + \text{Aq} = 100$ $\text{Fe} + \text{Br}_2 + \text{Aq} = 78$ $\text{Fe} + \text{O} + \text{H}_2\text{O} = 68$ $\text{Fe} + \text{O}_2 + \text{SO}_2 + 2\text{H}_2\text{O} = 169$	$\text{Co} + \text{Cl}_2 + \text{Aq} = 95$ $\text{Co} + \text{Br}_2 + \text{Aq} = 73$ $\text{Co} + \text{O} + \text{H}_2\text{O} = 63$ $\text{Co} + \text{O}_2 + \text{SO}_2 + 2\text{H}_2\text{O} = 163$	
$\text{LiCl}, \text{NaCl}, \text{KCl}$	$(\text{Li}, \text{Cl}) = 93.8$	$(\text{Ca}, \text{Cl}) = 97.7$	$(\text{K}, \text{Cl}) = 105.6$

Chemically similar compounds decompose at nearly the same temperature.

Since in general the atoms in chemically similar molecules are attracted together with nearly the same force, we should expect that if two chemically similar compounds AC, BC, be heated up, the degree of kinetic energy which suffices to part C from A in the one compound, will also be sufficient to part C from B in the other. But the degree of kinetic energy possessed by the atoms in general depends upon the temperature.

So that both compounds should begin to decompose about the same temperature.

The following data shows, that in general this is so.

It will be noticed, that the more closely allied chemically are the compounds the nearer the temperature at which they decompose. The theory is incomplete in the same particular as the theory of the last section.

For the same reason, chemically similar compounds are reduced by reducing agents such as H or CO about the same temperature.

Chemically similar compounds to be contrasted.	Temperature at which they decompose.
B ₂ O ₃ and SiO ₂	Both stable at the highest temperatures.
Co ₃ O ₄ and Ni ₂ O ₃	Decompose to Ni and Co at the melting point of Pt.
RuO ₄ and OsO ₄	RuO ₄ decomposes at 106°, OsO ₄ at a somewhat higher temp°.
MoO ₃ , WO ₃ , UO ₃	MoO ₃ is partially converted into the blue oxide (Mo ₂ O ₅) at 1750°. WO ₃ undergoes the same transformation at a somewhat higher temperature. UO ₃ gives U ₂ O ₅ at 1750°.
Ag ₂ O and Au ₂ O	Ag ₂ O is completely decomposed at 290°. Au ₂ O at 250°.
HgO, PtO and PdO	All decompose at a red heat.
MgO, ZnO, CdO	All stable at 1750°.
Al ₂ O ₃ , Ga ₂ O ₃ , In ₂ O ₃	All stable at the melting point of platinum.
Sb ₂ O ₅ , and Bi ₂ O ₅	Both decompose to lower oxides between 250° and 300°.
SO ₃ , SeO ₃ , and TeO ₃	All decompose to the di-oxide at a red heat.
Mn ₂ O ₃ and Fe ₂ O ₃	At a white heat both decompose into the tetroxides Fe ₃ O ₄ and Mn ₃ O ₄ .

Chemically similar compounds are almost always physically similar.

Compounds which react chemically in the same way, also exhibit a very close physical resemblance to each other, agreeing, for example, as regards colour, appearance, fusibility, volatility, solubility &c.

For example, BCl₃, SiCl₄, both react in the same way with the same reagents, and betray the greatest physical resemblance, both being colourless, very mobile, volatile liquids. NaOH

reacts in the same way as KOH, and both betray the greatest physical similarity, eg. both are white non-crystalline solids, both are hard to volatilise, both dissolve readily in H_2O &c. &c.

This fact makes one believe that same causes which determine the chemical properties of compounds also determine their physical properties.

But (as we have seen) it is the chemical forces at play within the molecule which determine the chemical properties of the compound. We conclude that the volatility, solubility, fusibility &c., of compounds is determined by these same chemical forces.

Since the fusibility and volatility of compounds is decided by the magnitude of the attractive forces which the molecules exert on each other, we deduce that the external attractive force which exists between molecule and molecule is in the main determined by the inner attractive forces which hold the atoms together in the molecule. We will come back to this point again.

The elements themselves are a special class of compounds whose molecules consist of atoms of the same kind.

For example, oxygen gas O_2 and ozone O_3 may be regarded as two different compounds formed out of oxygen atoms. It follows, then, as a particular case of the preceding generalisation, that those elementary bodies which resemble each other most closely as regards the way that they react chemically are precisely those which approach each other most closely in their physical behaviour. For example the three elements Fe, Co and Ni. resemble each other very closely as regards the way they react.

Physically also they resemble each other very closely — approaching each other even as regards such remotely connected physical attributes as magnetism and capacity for taking a high polish. The series of the halogens furnish an admirable example of the fact that the more closely do elements approach each other in their chemical behaviour, the more closely do they approach each other in their physical properties. (Contrast Cl with Br); and the that conversely a wide difference in chemical character is attended with a corresponding wide difference in physical properties (contrast fluorine with iodine). The Periodic

Law, which asserts that the properties of an element both chemical and physical, are regulated by the magnitude of its atomic weight, announces at the same time that these two sets of properties are not independent of each other, but that the same cause which determines the one determines the other. We will come back to this point again.

Influence of valence in determining chemical similarity.

We will now make a few remarks on the part valency plays in determining the chemical similarity of elements. It is not a self-obvious fact that the chemical and physical properties of an element depends solely upon the force with which its atoms attract other elementary atoms. In fact at the present time there exists a vague idea that the chemical similarity of elements depends in some way upon a capacity for building up compounds of the same type, an idea which gave rise to the sarcasm which appeared in Liebig's *Annalen* for 1840 in the form of a letter in which the chemical public is informed that the writer has succeeded in replacing in manganese acetate, not only the hydrogen by chlorine, but also the metal, and finally the oxygen and carbon too; the product, although consisting of chlorine only, exhibited all the characteristic properties of the original salt! *)

But since a capacity for building up compounds of the same type depends upon a capacity for acting with the same degree of valence, this idea is nothing less than the conception that the chemical similarity of elements depends in some way upon a capacity for acting with the same degree of valence.

As we have seen, however, equality of valence has little or nothing to do with chemical similarity. Compare, for example, the chemically similar elements B and Si, Fe and W, Pb and TL, Au and Pt &c.

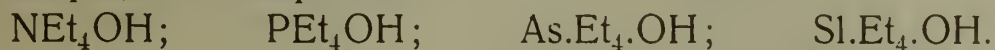
It has however, this result:

If two atoms A and B possess the same shape — that is possesses the same number of valency points (or centres of attraction

*) See Schloremmer's *Development of Organic Chemistry* p. 45.

arranged in the same manner over the surface of the atoms, then there results a mechanical similarity between the compounds of such elements, because in this case the compounds built up by both A and B consist of the same number of atoms arranged in the same way around the central atoms A and B. For example Mn and S are quite unlike chemically, yet both produce a series of compounds viz. R_2MnO_4 and R_2SO_4 which are chemically of the same type and isomorphous. The reason of this is, of course, that the atoms in both compounds are arranged in the same way around the Mn and S, and so the molecules have both the same shape. Yet the two compounds are chemically quite unlike. A still better example is that of $HMnO_4$ and $HClO_4$. No two elements could very well differ more in every way than Mn and Cl; yet in both the permanganates and perchlorates we have the same atoms arranged in the same way around the central Mn and Cl atoms, and this serves to give a mechanical similarity to the shapes of the molecule of corresponding perchlorates and permanganates.

If in addition to this mechanical similarity of construction the same atoms are attracted to the central atom with nearly the same intensity of force, this mechanical similarity becomes converted into a real chemical and physical similarity and the resemblance in properties may become very remarkable compare, for example, the compounds:



Section 3.

We will now proceed to illustrate by the individual study of the chemical reactions and behaviour of chemically similar elements and compounds the general conclusions arrived at in the preceding pages, namely:

1. That chemically similar elements invariably attract the same radicles with proportional intensities of force.
2. That the more nearly equal is the force with which the two elements attract the same radicles, the more closely allied chemically are the two elements.
3. That chemical similarity is invariably accompanied by physical similarity, and therefore, that the same factors (namely the affinities) which determine the chemical properties of an element or compound, must also determine its physical properties.
4. That the volatility, fusibility, solubility &c. depend almost entirely upon the attractive forces the atoms exert and not to any very great extent upon their molecular weight.

Incidentally we will show further:

5. That chemically unstable substances are as a whole characterised by their volatility and fusibility; chemically stable substances by their involatility and infusibility.
 6. Compounds of high valency grade are usually characterised by their volatility; compounds of low valency grade by their involatility.
-

The causes of the analogy between fluorine and oxygen.

Moissan some years ago (Bull. Soc. Chim., 1891, [3], v., 880) pointed out that, of all the halogens, fluorine is the one which resembles oxygen most closely in its general properties and in its compounds.

Being curious to know what it is that causes fluorine to resemble oxygen more closely than chlorine or bromine does, I proposed to myself the following questions:

A. Does not fluorine resemble oxygen more closely than chlorine resembles oxygen, because the fluorine approaches the oxygen more closely than the chlorine does, as regards the intensity of the force with which it attracts a given radicle? In other words, does not the chemical similarity of these two elements arise from the fact that they both attract the same radicles with nearly the same intensity of force?

B. Seeing that chemically similar elements and compounds, as a rule, have about the same degree of volatility and fusibility, is not this because there is a connection between the intensity of the chemical forces which an atom is capable of exerting and the degree of volatility of the compounds into which it enters? And in particular, would not this connection exhibit itself among the fluorides, chlorides, and oxides, in such a manner that those compounds which approach each other nearest in the intensity of the force with which the atoms in the molecules are attracted together, be those which approach each other nearest as regards fusibility and volatility?

That is to say, is it not the internal atomic forces in the molecule which determine the external forces with which the molecules themselves are attracted together?

The answer to both questions is in the affirmative, as will be seen from the following data:

A. First we will show, that fluorine and oxygen approach each other more closely in the intensity of the force with which they attract the same radicles than do chlorine and oxygen.

This may be established by three lines of argument:

- a) That founded on a comparison of the heats of formation of corresponding fluorides, chlorides, and oxides.
- b) That founded on the fact that O and F both tend to make an element with which they combine exhibit a higher grade of valence than Cl can make it exhibit.
- c) That founded on the chemical stability of corresponding fluorides, chlorides, bromides.

We will consider each briefly.

a) The heats of formation of the fluorides (so far as they are known) stand closer to the heats of formation of the corresponding oxides than to those of the corresponding chlorides. Thus, arguing that the intensity of force which holds the atoms together in the fluorides stands nearer to that which hold the atoms together in the corresponding oxides than in the corresponding chlorides.

For example, we have:

$$(H, Cl) = 22; \quad (H, F) = 37.6; \quad (H, O^{1/2}) = 34.2.$$

b) Oxygen and fluorine both resemble each other in that they tend to make the elements with which they combine exhibit a higher grade of valence than Cl can make them exhibit.

For example, the stablest oxide of Mn at ordinary temperatures is Mn_2O_3 . Also, the stablest fluoride is MnF_3 , whereas the stablest chloride is $MnCl_2$, $MnCl_3$ being an excessively unstable body spontaneously decomposing at ordinary temperatures to $MnCl_2$ and Cl. Again, SO_3 is at ordinary temperatures a quite stable body, not parting with O below a red heat. Also SF_6 is a very stable body. Whereas SCl_6 is too unstable to exist at ordinary temperatures, and SCl_4 is only capable of existing below $-20^\circ C$. Similarly, P_2O_5 is at ordinary temperatures by far the stablest oxide of P; so also PF_5 is the stablest fluoride of P; on the other hand, PCl_5 is easily decomposed to PCl_3 .

The stablest oxide of I is I_2O_5 , and the stablest fluoride is IF_5 . But ICl_5 is so unstable that it seems incapable of existing at ordinary temperatures. ICl_3 is also unstable, easily decomposing when heated. Only ICl seems to be stable enough to

bear heating. (Notice that the fluorides follow the oxides and not the chlorides as regards stability).

These facts can be best interpreted to mean that both O and F exert nearly the same intensity of force on an element, so that when O is capable of making the element give rise to a stable compound of a high valency grade, F is also capable of doing the same thing.

On the other hand the intensity of the force exerted by Cl on the same element is much less, so that the corresponding high valency compounds of Cl are much less stable than those of O and F.

c) The chemical stability of compounds depends upon the intensity of the forces with which the atoms are attracted together in the molecule. We will show that when we contrast an oxide and the corresponding fluoride, on the one hand, with the same oxide and the corresponding chloride on the other, the oxide and fluoride approach each other much more closely as regards their stability than do the oxide and chloride. In fact, when the oxides of an element are unstable and the chlorides stable, then the fluorides follow oxides in being unstable. And conversely, when the oxides are stable and the chlorides are unstable, the fluorides follow the oxides in being stable.

So that O and F approach each other more closely than do O and Cl in the intensity of the force with which they attract the same radicles. We will now illustrate this.

1. The following examples show that when the oxides are less stable than the chlorides, the fluorides are also less stable than the chlorides:

Na_2O , NaCl , NaF . — The fact that the heat evolved when Na combines with an equivalent of O is much less than the heat evolved when Na combines with an equivalent of Cl, $[(\text{Na}, \text{O}^{1/2}) = 49.8$ ($\text{Na}, \text{Cl}) = 97.7]$, shows that Cl is attracted to the Na with a greater force than is O. The fact that NaCl is hardly acted on at all superheated steam, whereas NaF is partially decomposed, indicates that in NaF the F is attracted to the Na with a force less than that with which the Cl is in NaCl .

K_2O , KCl , KF . — We have $(K, O^{1/2}) = 47.45$, $(K, Cl) = 105.6$, so that KCl is very much more stable than K_2O . Also KCl is very much more stable than KF ; for water at ordinary temperatures is capable of decomposing KF , whereas KCl is only decomposed by water at a red heat.

Ag_2O , $AgCl$, AgF . — We have $(Ag, Cl) = 29.00$, $(Ag, O^{1/2}) = 2.950$, which indicates that $AgCl$ is very much more stable than Ag_2O . Again, Ag_2O is completely decomposed at 290° , whereas $AgCl$ is not decomposed at 1735° (white heat).

Similarly, AgF is like Ag_2O , much less stable than $AgCl$, being completely decomposed to Ag , when heated in the air.

AuF_3 in this respect resembles AgF , but is even more unstable than this body, because Au_2O_3 is more unstable than Ag_2O . See also below, HgF_2 .

CuO , $CuCl_2$, CuF_2 . — We have $(Cu^{1/2}, Cl) = 25.8$, $(Cu^{1/2}, O^{1/2}) = 18.6$. So that Cl is more strongly attracted by Cu than is O .

So also the fluorides of Cu are very much more unstable than the chlorides, $CuF_2 \cdot 2H_2O$, for example, spontaneously decomposing in three or four days.

HgO , $HgCl_2$, HgF_2 . — The oxides of Hg are less stable than the chlorides. For example, $HgCl_2$ can be vaporised without decomposition, whereas HgO easily decomposes when heated. The same appears from the heats of formation:

$$\begin{aligned} (Hg^{1/2}, O^{1/2}) &= 11.00, & (Hg^{1/2}, Cl) &= 27.24 \\ (Hg, O^{1/2}) &= 12.43, & (Hg, Cl) &= 32.60 \end{aligned}$$

Also the fluorides of Hg are much less stable than the chlorides, both towards the action of water and of heat.

Thus the hydrated fluoride is decomposed at only 30° , and HgF_2 is decomposed at ordinary temperatures by H_2O .

HgF is decomposed to Hg and F when heated above 200° .

2. The following examples show that when the oxides are more stable than the chlorides, the fluorides are also more stable than the chlorides.

SO_3 , SCl_6 , SF_6 . — SO_3 is a quite stable substance at ordinary temperatures, and only decomposes at a red heat. SCl_6 is at ordinary temperatures too unstable to exist, even SCl_4 only exists below -20° . SF_6 is like SO_3 quite stable even at a red heat.

B_2O_3 , BCl_3 , BF_3 . — We have $(\text{B}^{1/3}, \text{O}^{1/2}) = 52.8$. $(\text{B}^{1/3}, \text{Cl}) = 34.6$, showing that B_2O_3 is very much more stable than BCl_3 . A comparison of the chemical behaviour of the two substances confirms this conclusion. BCl_3 , for example, is easily decomposed by heat and various chemical reagents, such as water; B_2O_3 , however, is stable at the highest temperatures, and is not decomposed by heating with carbon.

Similarly, BF_3 is very much more stable than BCl_3 . It is not (like BCl_3) decomposed by electric sparks, nor by Fe at a red heat.

Al_2O_3 , AlCl_3 , AlF_3 . — Al_2O_3 is very much more stable than AlCl_3 . Also AlF_3 is very much more stable than AlCl_3 being, unlike the latter, unacted upon by air, acids or alkalis. AlF_3 resembles Al_2O_3 rather than AlCl_3 in appearance, properties and stability.

Mn_2O_3 , MnCl_3 , MnF_3 . — Mn_2O_3 and MnF_3 are both, at ordinary temperatures, perfectly stable bodies. MnCl_3 , however, is excessively unstable, spontaneously decomposing at ordinary temperatures into MnCl_2 and Cl.

The first question we have proposed must therefore be answered in the affirmative, namely, fluorine resembles oxygen more closely than does chlorine, because the fluorine atom attracts a given radicle with an intensity of force which approaches nearer that which oxygen exerts on the same radicle than does that which chlorine exerts.

And therefore that the chemical similarity of these two elements arises from the fact that both attract the same radicles with nearly the same intensity of force.

B. We now proceed to deal with the second question.

The accompanying tables show that the corresponding fluorides and oxides approach each other more closely as regards volatility than do the corresponding chlorides and oxides;

Table 1. shows that non-metallic fluorides are more volatile than the non-metallic chlorides.

Table 2. shows that the non-metallic oxides are more volatile than the non-metallic chlorides.

Table 3. shows that metallic fluorides are usually less volatile than the corresponding metallic chlorides.

Table 4. shows that the metallic oxides are also less volatile than the corresponding metallic chlorides.

In other words, those compounds which approach each other nearest in the intensity of force with which the atoms are attracted together in the molecule (viz., the oxides and fluorides) are precisely those which approach each other nearest as regards volatility and fusibility.

That is to say, it is the intensity of internal atomic forces with which the atoms are attracted together in the molecule which determines the intensity of the external attractive force between molecule and molecule, and therefore the volatility of the compound.

This seems a very important conclusion.

A wider research given later and embracing the compounds of all the elements will convince the reader that this is true in its generality.

Table 1.

Showing that non-metallic fluorides are more volatile than non-metallic chlorides.

Compound	Physical state	Volatility
PF_3	Gas	—
PCl_3	Liquid	Boils at 78°
PF_5	Gas	—
PCl_5	Solid	Sublimes at about 147°
POF_3	Gas	—
POCl_3	Liquid	Boils at 107.5°
SiF_4	Gas	Boils at — 107°
SiCl_4	Liquid	Boils at 59°
BF_3	Gas	—
BCl_3	Liquid	18.5°

Compound	Physical state	Volatility
CF ₄	Gas	—
CCl ₄	Liquid	78 °
SF ₆	Gas	Boils a little above — 55 °
SCl ₂	Liquid	Boils at +139 °
SOF ₂	Gas	„ — 32 °
SOCl ₂	Liquid	„ + 78.8 °
SO ₂ F ₂	Gas	„ — 52 °
SO ₂ Cl ₂	Liquid	„ + 82 °
AsF ₃	Liquid	„ 63 °
AsCl ₃	Liquid	„ 130 °

Table 2.

Showing that non-metallic oxides are usually more volatile than the corresponding chlorides.

(Data is largely taken from Henry, Phil. Mag., 1885, [5j, XX., 81).

Compound	Physical state	Volatility
OO	Perfect gas, formerly considered permanent	B.p. — 183 ° C
OCl ₂	Gas, easily liquefied	„ — 17 °
SO ₂	Gas	„ — 10 °
SOCl ₂	Liquid	„ + 82 °
SO ₃	Solid	„ 46 °
SO ₂ Cl ₂	Liquid	„ 82 °
CO ₂	Gas	Boils — 78 °
COCl ₂	Liquid	„ 8 °
CCl ₄	Liquid	„ 76 °
C ₂ Cl ₄ O	Liquid	„ 118 °
C ₂ Cl ₆	Solid	„ 182 °
POCl ₃	Liquid	„ 110 °
PCl ₅	Solid	„ 148 °
CO ₂	Gas	„ — 78 °
CCl ₄	Liquid	„ + 76 °

Table 3.

Showing that the metallic fluorides are usually less fusible than the corresponding chlorides.

Compound	Physical state	Fusibility
		Melting-point
LiF	Solid	801 ⁰
LiCl	"	598 ⁰
NaF	"	902 ⁰
NaCl	"	772 ⁰
KF	"	789 ⁰
KCl	"	738 ⁰
RbF	"	753 ⁰
RbCl	"	719 ⁰
CuF	"	908 ⁰
CuCl	"	434 ⁰
AgF	"	435 ⁰
AgCl	"	457 ⁰
CaF ₂	"	902 ⁰
CaCl ₂	"	719 ⁰
SnF ₂	"	902 ⁰
SnCl ₂	"	825 ⁰
BaF ₂	"	908 ⁰
BaCl ₂	"	860 ⁰
MgF ₂	"	908 ⁰
MgCl ₂	"	708 ⁰
ZnF ₂	"	734 ⁰
ZnCl ₂	"	262 ⁰
CdF ₂	"	520 ⁰
CdCl ₂	"	541 ⁰
SbF ₃	"	296 ⁰
SbCl ₃	"	73.2 ⁰
ZrF ₄	"	White heat
ZrCl ₄	"	400 ⁰

Table 4.

Showing that metallic oxides are usually less volatile and fusible than the corresponding chlorides.

(Data largely taken from a compilation by Henry, loc. cit.).

Compound	Physical state	Fusibility	Volatility
NbCl ₅	Solid	Fuses at 194 °	Boils at 240.5 °
Nb ₂ O ₅	"	Infusible	Fixed
TaCl ₅	"	Fuses at 211.3 °	Boils at 241.6 °
Ta ₂ O ₅	"	Infusible	Fixed
Al ₂ Cl ₆	"	Very fusible	Boils at 180 °
Al ₂ O ₃	"	Fusible in O.H flame	Fixed
FeCl ₃	"	Fuses at 306 °	Easily volatile
Fe ₂ O ₃	"	Infusible	Fixed
CrCl ₃	"	—	Volatile
Cr ₂ O ₃	"	Infusible	Fixed
CrO ₂ Cl ₂	Liquid	—	Boils at 118 °
CrO ₃	Solid	Fuses about 200 °	Decomposes.
WCl ₅	"	Fuses at 248 °	Boils at 275.6 °
WCl ₆	"	" 275 °	" 346.7 °
WCl ₄ O	"	" 210.4 °	" 127.5 °
WO ₃	"	" a red heat	Fixed
VCl ₄	Liquid	Does not solidify at — 18 °	Boils at 154 °
VO ₂	Solid	—	—
VOCl ₃	Liquid	Does not solidify at — 15 °	Boils at 126.7 °
TeCl ₄	Solid	Fuses at 224 °	Boils at 414 °
TeO ₂	"	Fusible	Less volatile than tellurium
AsCl ₃	Liquid	Does not solidify at — 29 °	Boils at 134 °
As ₂ O ₃	Solid	Volatile without fusion	" 200 °
SbCl ₃	"	Fuses at 73.2 °	Boils at 225 °
Sb ₂ O ₃	"	" red heat	Volatile below 156 °

Compound	Physical state	Fusibility	Volatility
SbCl_5	Liquid	Solid at 0°	Volatilises into SbCl_3 and Cl_2
Sb_2O_5	Solid	Non-fusible	Non-volatile
BiCl_3	"	Fuses at 227°	Boils at $427\text{--}439^\circ$
Bi_2O_3	"	Fusible	Fixed
HgCl_2	"	Fuses at 265°	Boils at 295°
HgO	"	Infusible	Decomposed at red heat
Hg_2Cl_2	"	Sublimes at $400\text{--}500^\circ$ without melting	—
Hg_2O	"	Infusible	Decomposes
Cu_2Cl_2	"	Fuses at 434°	Boils at $954\text{--}1032^\circ$
Cu_2O	"	" a red heat	Fixed
CuCl_2	"	Fuses at 498°	Decomposes
CuO	"	Fuses at bright red heat with decomposition	"
PbCl_2	"	Fuses at 498°	Boils at $861\text{--}954^\circ$
PbO	"	Fuses about a red heat	Volatile at white heat
AgCl	"	Fuses at 451°	—
Ag_2O	"	Infusible	Decomposes
CaCl_2	"	Fuses at 719°	—
CaO	"	Infusible	Fixed
SnCl_2	"	Fuses at 825°	—
SnO	"	Infusible	Fixed
BaCl_2	"	Fuses above 860°	—
BaO	"	Fusible in O.H flame	Fixed
MgCl_2	"	Melts at 708°	Volatile
MgO	"	Infusible	Fixed
ZnCl_2	"	Fuses at 262°	Boils at $676\text{--}683^\circ$
ZnO	"	Infusible	Fixed
CdCl_2	"	Fuses at 541°	Boils at $861\text{--}954^\circ$
CdO	"	Infusible	Fixed
UCl_4	"	—	Volatile
UO_2	"	Infusible	Fixed

Causes of the chemical similarity of Boron and Silicon.

We will now study the corresponding compounds of boron and silicon in order to show that both atoms owe their chemical similarity to the fact that they attract the same radicles with the same intensity of force.

B_2O_3 and SiO_2 .

B_2O_3	SiO_2	Inference
1. S.G. 1.75 to 1.83	1. S.G. 2.2 to 2.6.	
2. A semi-transparent, colourless, inodorous, glass-like solid.	2. A transparent, colourless, inodorous, glass-like solid.	
3. Melts at a bright red heat (about 600°). Volatilises at a very high temp ^o . Volatilises slightly in steam.	3. Melts in the O.H flame to a colour-liquid. Volatilises at a temperature whereat Platinum boils. Silicon is slightly volatile in steam.	Physically the two bodies closely resemble each other; both are difficult to fuse or volatilise; both are non-conductors of electricity and transparent.
4. Non-conductor of electricity.	4. Non-conductor of electricity.	
5. B_2O_3 is a very stable compound. It is not decomposed by heating with charcoal.	5. SiO_2 is a very stable compound. It is not decomposed by heating with charcoal.	5. The O atoms are attracted by the B and the Si with a very intense force.

B_2O_3	SiO_2	Inference
6. Heat of formation is $(B^{1/3}, O^{1/2}) = 52.8.$	6. Heat of formation is $(Si^{1/4}, O^{1/2}) = 52.7.$	6. The O is attracted by the B and the Si with nearly the same intensity of force.
7. A mixture of B_2O_3 and C heated in chlorine or Br yields BCl_3 or BBr_3 .	7. A mixture of SiO_2 and C heated in chlorine or Br gives $SiCl_4$ or $SiBr_4$.	Both substances seem to be decomposed by the same reagents at about the same temp ^o range, thus confirming the conclusion that the atoms are attracted together in the molecule with about the same intensity of force.
8. Reacts with most metallic oxides at high temps ^o to form borates, which are characterised by their stability and involatility.	8. Reacts with most metallic oxides at a high temp ^o , to form silicates which are characterised by their stability and involatility.	
9. B_2O_3 is the anhydride of a very feeble acid.	9. SiO_2 is the anhydride of a very feeble acid.	
10. But appears to show a feeble basic character in its reactions with certain acids. Eg. it unites with phosphoric acid to form the compound $B_2O_5.P_2O_5$.	10. But appears to show a feebly basic character in its reactions with certain acids; eg. it reacts with molten meta-phosphoric acid to form the compound $SiO_2.P_2O_5$.	Both compounds seem to exert external forces of the same nature and intensity, so that they enter into the same combinations.

The correspondence is very remarkable. Notice

1. That the oxygen is attacked with nearly the same intensity of force both to the B and the Si, as is judged from the fact

that any influence which seems capable of removing O from the one, can also remove O from the other body; and also from the fact, that they have nearly the same H.F.

2. That they are physically similar.
3. That as regards fusibility and volatility they resemble each other — both for example volatilise slightly when distilled with steam.

BCl_3 and SiCl_4 .

BCl_3	SiCl_4	Inference
1. Mol. wgt. 117.08.	1. Mol. wgt. 169.76.	<p>These similar methods of formation show that forces of the same intensity and nature are at work in producing these two compounds.</p> <p>Both bodies approach each other very closely as regards their fusibility and volatility.</p> <p>Both, for example, are liquids at 18°, and gaseous at 60°.</p> <p>Both substances are decomposed by the same reagents at about the same temp^o</p>
2. S.G. = 1.35.	2. S.G. = 1.52.	
3. Formed:	3. Formed:	
a) By direct union of B and Cl.	a) By direct union of Si and Cl.	
b) By the action of Cl with B_2O_3 and C at a red heat.	b) By the action of Cl with SiO_2 and C at a red heat.	
c) By acting on B with dry HCl.	c) By acting on Si with dry HCl.	
4. A colourless, highly refractive liquid. Boils at 18°C (760).	4. A colourless, very clear, liquid. Boils at 57.5 and at 760 .	
5. Fumes in the air with decomposition.	5. Fumes in the air with decomposition.	
6. Decomposed by water to form HCl and H_3BO_3 .	6. Decomposed by water to form HCl and H_2SiO_3 .	

BCl_3	SiCl_4	Inference
7. Decomposed when heated with Na, NaCl being formed, and B separating.	7. Decomposed by heating with Na, NaCl being formed and Si separating.	ranges; the atoms therefore are attracted together in the molecule with nearly the same intensity of force.
8. The heat of formation is: $(\text{B}^1_3, \text{Cl}) = 34.6.$	8. The heat of formation is: $(\text{Si}^1_4, \text{Cl}) = 39.4.$	The intensity of force with which the atoms are attracted together in the molecule is nearly the same.

Here again the correspondence is very remarkable.

Notice:

1. That the chlorine is attacked with nearly the same intensity of force both to the B and to the Si, as is deduced from the fact that any reagent which is capable of decomposing the one, is also capable of decomposing the other; and also from the fact that they have H.F's of the some order of magnitude.
2. That they are physically similar.
3. That as regards fusibility and volatility they resemble each other — both, for example, being liquids at 18° and gases at 60° . The fusibility and volatility in fact seems to depend much less upon the chemical forces than upon the magnitude of the molecule.

BF_3 and SiF_4 .

BF_3	SiF_4	Inferences
1. Mol. wgt. 68.27. V.D. 33.7.	1. Mol. wgt. 104.3. V.D. 51.9.	

BF_3	SiF_4	Inferences
2. Prepared by heating together B_2O_3 , CaF_2 , and H_2SO_4 .	2. Prepared by heating together SiO_2 , CaF_2 and H_2SO_4 .	This similar method of formation shows that forces of the same intensity and nature come into play in the production of these two compounds.
3. Colourless gas, with a suffocating odour. Condenses to a limpid liquid at -110° and a strong pressure.	3. Colourless gas, with a disagreeable odour. Condenses to a colourless mobile liquid at -106.5° and 9 atmospheres pressure.	
4. With dry NH_3 gas BF_3 forms a white opaque solid $\text{BF}_3 \cdot \text{NH}_3$.	4. With dry NH_3 gas, SiF_4 forms a white, crystalline compd. $\text{SiF}_4 \cdot 2\text{NH}_3$.	Both bodies approach each other very closely in volatility; both are gases at ordinary temps ^o ; Both are liquids at -110° , and gases at -107°C in spite of mol. weights of very different magnitudes.
5. Alkaline and alkaline earth metals react at a red heat forming boro-fluorides and B.	5. K and Fe when hot burn in SiF_4 forming fluorides and Si.	
6. Water absorbs BF_3 in large quantities. forming $\text{B}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ and HBF_4 which is a strongly acid liquid.	6. Water absorbs SiF_4 in large quantities, forming $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ and H_2SiF_6 , which is a strongly acid liquid.	Both bodies approach each other very closely as regards the way they react with the same reagents.

Here again the resemblance is quite remarkable. Both react in the same way chemically; the same reagents which decompose the one with also decompose the other.

The Fluorine therefore must be attracted both by the B and Si with nearly the same intensity of force.

Closely connected with this is the fact that both possess nearly the same degree of volatility.

A study of the corresponding compounds of Boron and Silicon thus shows that they attract the 3 radicles Cl, F and O with nearly the same intensity of force, each to each. A more extended research will convince the reader that the same is true for the other radicles also.

In fact the chemical similarity of Boron and Silicon arises from the fact that they attract the same radicles with the same intensity of force.

Here then are two atoms which are chemically similar and yet combine in different proportions with other elements eg. Boron forms BX_3 , Silicon forms SiX_4 .

This shows that the chemical similarity of elements, does not depend upon the degree of valence they manifest, but upon the intensity of force with which they attract other radicles.

These compounds of Boron and Silicon furnish an admirable illustration of the intimate connections, which exists between the chemical forces which bind together the atoms in the molecule, and the volatility and fusibility of these bodies.

Thus BCl_3 and B_2O_3 differ widely in stability and also in fusibility and volatility.

Also $SiCl_4$ and SiO_2 differ widely in stability and also in fusibility and volatility. But BCl_3 and $SiCl_4$ have almost the same degree of stability and of volatility and fusibility.

Similarity B_2O_3 has nearly the same degree of stability and also of volatility and fusibility.

The molecular weights have little to do with the volatility and fusibility of compounds in comparison with the chemical forces.

The chemical analogy of water and hydrofluoric acid.

We have just seen that of all the halogens, fluorine is the one which approaches oxygen most closely in the intensity of force with which it attracts other atoms. It is also the one whose halogen hydride approaches nearest to oxygen hydride (water) in chemical and physical properties. Consider for example the following table:

Substance	Boiling point	Melting point	Range of fluidity (B.Pt.—M.Pt.)	Equivalent heat of formation
HI	— 34.1°	— 50.8°	16.7°	— 6.036
HBr	— 64.9°	— 87.9°	23°	+ 8.44
HCl	— 83.7°	— 111.1°	27.4°	+ 22.0
HF	+ 19.44°	— 92.3°	111.74°	37.6
H ₂ O	100°	0°	100°	34.2

Of all these hydrides, HF is the one whose heat of formation most nearly approaches that of water (34.2 : 37.2). It is also the one which in all its physical properties and in most of its chemical properties most closely resembles water.

Notice:

That its boiling point lies nearest to that of water;
that its range of fluidity (i.e. difference between B.Pt and M.Pt) approaches nearest to that of water (H₂O = 100°, HF = 111.74°);

that while all the other hydrides are so volatile as to be gaseous at ordinary temps°, water and HF are colourless mobile liquids.

This shows how very greatly the volatility of a substance (and perhaps its range of fluidity) depends upon the intensity of the forces with which the atoms are attracted together in the molecule (as shown by the magnitude of the heat of formation).

Liquids in general which differ very widely as regards the intensity of this force, differ also very widely in Volatility.

To show the resemblance between water and hydrofluoric acid, we will contrast their properties:

H ₂ O	HF	Inferences
<p>1. At an ordinary temp^o water is a clear, transparent mobile liquid. Boils at 100^o. Freezes at 0^o.</p> <p>2. Water consists of complex molecules at ordinary temps^o. According to Ramsay and Shields mol. is (H₂O)₄, according to other authors (H₂O)₂.</p>	<p>1. At an ordinary temp^o HF is a clear, transparent colourless, mobile liquid. Boils at 19.44^o. Melts at -92.3^o.</p> <p>2. Complex molecules; probably varying in complexity from (HF)₄ to H₂F₂ and HF.</p>	<p>2. This is an example of the general rule that molecules of chemically similar elements produce corresponding compounds whose molecules are condensed together to the same extent. (Compare (B₂O₃)_n (SiO₂)_n : BCl₃, SiCl₄) presumably because the molecules of similar compounds attract each other with nearly the same intensity of force; this in it turn arises out of the fact that the atoms in similar compounds are attracted together with the same intensity of force in the molecule. It is the internal atomic chemi-</p>

H ₂ O	HF	Inferences
<p>3. Liquid water at ordinary temps⁰ does not react as a rule on metals or non-metals. It, however, reacts with the alkali metals at ordinary temps⁰.</p> <p>4. Liquid water reacts violently with many anhydrides eg. P₂O₅ and SO₃.</p> <p>5. H₂O does not decompose the chlorides of the alkali metals, but it decomposes chlorides of P, Sb, Ti.</p>	<p>3. Liquid HF at — 18° to — 29° does not as a rule react on metals or non-metals except the alkali metals.</p> <p>4. Liquid HF reacts violently with many anhydrides eg. P₂O₅ and SO₃.</p> <p>5. HF decomposes the chlorides of the alkali metals. And also the chlorides of P, Sb and Ti.</p>	<p>cal forces which determine the external molecular forces, and this in its turn determines the degree of molecular condensation.</p> <p>3. It seems as if HF is in the same condition at — 29° as water is at ordinary temps⁰.</p> <p>5. This shows that fluorine attracts positive radicles with a greater intensity of force than does oxygen. This is also evident not only from the greater heat of formation of HF over H₂O, but also from the fact that fluorine spontaneously decomposes water forming HF and O₃. Fluorine attracts H with a greater intensity of force than does O.</p>

It must be remembered that we have a very exaggerated idea of the difference between water and the halogen acids principally because they happen to effect human beings in very different ways — a pure accident of personal constitution.

Causes of the Chemical Similarity of Molybdenum and Wolfram.

These two elements also furnish a good illustration of the fact that the chemical similarity of elements is determined almost entirely by the proportionality of the forces with which they attract other radicles. Their reactions have been recently studied by Ehrenfeld (j. Amer. Chem. Soc. 1895, 17. 381—397) and Smith; (Zeit-Anorg. chem. I. 360—363. Smith and Oberholtzen. Zeit-Anorg. chem. 5, 63—68) and we have in consequence a good knowledge of their comparative reactions. The chemical forces which W exerts are somewhat more intense than the corresponding forces which Mo exerts, but are proportional to them, each to each.

It is from this fact arises the slight differences as regards chemical behaviour which exists between the two bodies. Were the chemical forces of precisely the same intensity, both substances would react in precisely the same way.

W	Mo	Inferences
1. When finely powdered W is heated in a stream of NO it oxidises. The action commences below a red heat and the substance becomes red hot. The product is WO_3 .	1. With Mo a similar reaction takes place, but the action is less energetic and MoO_2 is produced.	1. These reactions illustrate very well how precisely upon the force with which Mo and W attract other radicles depends their degree of chemical similarity. Thus almost
2. When heated with N_2O , W goes into	2. Mo heated in the same way required	

W	Mo	Inferences
<p>WO₃, but the action is less energetic than with NO.</p>	<p>a full red heat before any action took place, the product being MoO₂.</p>	<p>every reaction which W is capable of bringing about can also be brought about by Mo, because it attracts the same radicles as W with very nearly the same force. The reactions show that W attracts O with a slightly greater intensity of force than does Mo. This fact comes out more clearly when we study their oxides.</p>
<p>3. With NO₂ and W, the action commences at about 300° — 350° and then proceeds rapidly, WO₃ being formed.</p>	<p>3. With Mo the action begins at an incipient red heat MoO₃ is formed.</p>	
<p>4. With SO₂ W is slowly oxidised at a moderately high temp°, lower oxides being formed.</p>	<p>4. With Mo the action takes place only at the highest temp and MoO₃ is formed.</p>	
<p>5. W reduces a solution of FeCl₃ according to the equation $\text{FeCl}_3 + \text{W} = \text{WCl}_6 + 6\text{FeCl}_2$. But the reaction is extremely slow. There is a gradual increase in the amount of the Fe reduced roughly proportional to the time, but complete solution of the W cannot be obtained.</p>	<p>5. Mo^{tr} reduces a soln. of FeCl₃ according to the equation $6\text{FeCl}_3 + \text{Mo} = \text{MoCl}_6 + 6\text{FeCl}_2$. Complete reduction does not however take place in a measurable length of time.</p>	
<p>6. W precipitates Ag from AgNO₃. The action is a quanti-</p>	<p>6. Mo acts towards Ag and Au solutions very like W, the</p>	

W	Mo	Inferences
tative one, one atom of W precipitating 6 of Ag. Similary one atom of W precipitates 2 atoms of Au from AuCl_3 .	actions in the case of gold, being however somewhat quicker.	Notice that those reagents which do not effect W, also do not effect Mo, and those reagents which effect W also effect Mo. Thus showing that the chemical forces exerted by Mo and W are of the same intensity.
7. W has no action on a neutral, alkaline, or acid solution of PbNO_3 .	7. Mo has no action on a neutral, alkaline, or acid solution of PbNO_3 .	
8. Solutions of Bi and Cd are unaffected by W.	8. Solutions of Bi and Cd are unaffected by Mo.	
9. The chlorides of Pt, Pd and Rh only undergo partial reduction by W.	9. The chlorides of Pt, Pd and Rh only undergo partial reduction by W.	
10. W precipitates Cu from solutions of a Cu salt. But the action is not a complete one.	10. Mo precipitates Cu from solutions of a Cu salt, but the action is not a complete one.	
11. CO and NH_3 are without action on W.	11. CO & NH_3 are without action on Mo.	
12. When W is heated in CoCl_2 an orange red sublimate is formed.	12. When Mo is heated in CoCl_2 , a liquid sublimate is formed, which solidifies to a reddish brown mass melting below 100° .	Notice: a) That both reagents seem to act on W & Mo under the same conditi-

W	Mo	Inference
13. W when heated in sulphur chloride yields a red crystalline sublimate.	13. Mo when heated in sulphur chloride yields a reddish brown sublimate.	ons in a similar manner. b) That the products both agree as regards being easily volatile. The volatility seems to depend upon the equality in intensity of the chemical forces at play.

So for we have been dealing solely with the way which W and Mo react; and we have shown that to judge from their chemical reactions, both exert chemical forces of nearly the same intensity, those of W being somewhat more intense.

We will now show that both substances resemble each other physically — as regards volatility, fusibility, general appearance &c. &c.

Physical properties of Mo and W.

Mo	W	Remarks
1. Does not melt in the O.H flame at a temp. at which Pt melts.	1. Can with difficulty be melted in the O.H flame.	Both substances are characterised by their great infusibility and involatility; both melting at about the temp ⁰ at which iron melts.

Mo	W	Remarks
2. Fused Mo is an extremely hard, white lustrous metal. It is as malleable as iron, files and polishes readily.	2. Fused W is an extremely hard, white lustrous metal. It is as malleable as iron and files and polishes readily.	Both bodies resemble iron strongly in their physical properties.
3. When pure Mo is heated in carbon at about 1500° it undergoes cementation and becomes hard enough to scratch glass, and if heated to 300° and suddenly cooled in water, it becomes brittle and will scratch rock crystal. Mo in masses may thus be used as a deoxidising agent for overblown Bessemer Steel, and has the advantage that the oxide is volatile and an excess of metal which may remain with the iron is malleable like the latter and will acquire temper under the same conditions.	3. W behaves in a similar way.	Both W and Mo resemble each other and iron very remarkably in their physical properties.

Mo	W	Remarks
4. At. wgt. 95.9 Sp. grav. 8.5	4. At. wgt. 183.6 Sp. grav. 18.7	The atom of the one substance is twice as heavy as the atom of the other; yet this does not deter the two atoms from exerting chemical forces of the same intensity. The Sp. Gr. seems to depend upon the magnitude of the At. wgt. and not upon the chemical forces.

Since the chemical forces are nearly of the same intensity in both substances, while the atomic weights differ widely, those properties which depend upon the chemical forces will lie close together, those which depend upon the magnitude of the atoms will lie far apart.

We conclude:

- a) The fusibility, volatility, &c. depends more upon the chemical forces than upon the magnitude of the atoms;
- b) the sp. gravity depends more upon the magnitude of the atoms than upon the chemical forces.

We conclude with a comparative study of the trioxides of W and Mo. A minute study of these bodies is very instructive as an illustration of the fact that the chemical properties of a body depend entirely upon the intensity of the chemical forces exerted by the atoms.

WO_3	MoO_3	Inferences
1. WO_3 when heated with an equivalent weight of PCl_5 in an atmosphere of CO_2 , is converted into WCl_6 and WCl_5 and POCl_3 is evolved.	1. MoO_3 when heated with an equivalent weight of PCl_5 reacts at a lower temp ^o than does WO_3 and the reaction is more rapid and energetic. MoCl_5 is produced mixed with small quantities of lower chlorides.	1. The O is attached to the W with a somewhat greater intensity of force than it is to the Mo, since O is more easily parted from Mo in MoO_3 . Than from W in WO_3 .
2. WO_3 when heated in a stream of C_2H_4 , is slowly reduced at a red heat, a deep blue oxide being formed. (W_2O_5 ?)	2. MoO_3 when treated in a similar manner yields a bronze colored crystalline oxide of formula Mo_2O_5 .	2. MoO_3 and WO_3 are both reduced at a red heat, by the same reducing agent, thus showing that the O is held with about the same force in the two compounds.
3. When heated in a current of C_2H_2 , WO_3 is slowly reduced to a mixture of brown and blue oxides.	3. MoO_3 under the same circumstances is reduced somewhat more readily and Mo_2O_5 is obtained.	3. Shows that O is held with a somewhat feeble force by Mo than by W.
4. WO_3 is not reduced by CH_4 at the highest temp ^o of a Bunsen Burner, but at the full heat of a blast lamp, the tri-oxide is reduced to the blue oxide W_2O_5 .	4. MoO_3 is reduced to MoO_2 at the ordinary heat of a Bunsen Flame.	4. O is attached somewhat more strongly to the W than to the Mo.

WO_3	MoO_3	Inferences
<p>5. WO_3 when heated in OH_2 is reduced at about $125\text{--}150^\circ$. The product is a deep blue oxide of the composition W_3O_8 and contains about 2% of P mechanically mixed with it.</p>	<p>5. MoO_3 when immersed in PH_3 begins to show traces of reduction without the application of heat and when gently heated the action proceeds rapidly. A purple oxide Mo_2O_5 is formed which contains about 2% of P.</p>	<p>5. Here again the O seems to be attached to the W with a somewhat greater intensity of force than to the Mo.</p>
<p>6. With As the products are the same as with PH_3 but the reduction takes place more sluggishly.</p>	<p>6. With AsH_3 the products are the same as with PH_3, but the reduction takes place more sluggishly. As usual MoO_3 is more easily reduced than WoO_3.</p>	<p>6. The O is attached with a somewhat feebleness to the Mo then to the W in MoO_3.</p>
<p>7. NH_3 acts on WO_3 more energetically than PH_3 does. The products are very complicated.</p>	<p>7. NH_3 acts on MoO_3 more energetically than PH_3 does. But the products are complicated.</p>	<p>Notice that those reagents which react on WO_3 also react on MoO_3, and that those reagents which do not react in WO_3 also do not react on MoO_3. This shows how very nearly equal is the intensity of force with which the O is attached to the W and to the Mo</p>
<p>8. WO_3 is not effected by ethane. C_2H_6.</p>	<p>8. MoO_3 is not effected by ethane. C_2H_6.</p>	
<p>9. No action takes place when WO_3 is heated with SiCl_4 in an atmosphere of CO_2.</p>	<p>9. No action likewise takes place when MoO_3 is heated with SiCl_4 in CO_2.</p>	
<p>10. WO_3 is unchanged when heated in a stream of NO.</p>	<p>10. MoO_3 is unchanged when heated in a stream of NO.</p>	

WO_3	MoO_3	Inference
11. When WO_3 is heated with Al in a tube sealed at one end, no action takes place until a full red heat is reached, when there is a flash and a slight report, cracking the tube and scattering the contents.	11. With MoO_3 the action is similar and the blue oxide Mo_2O_5 is formed.	} in WO_3 and MoO_3 respectively.
12. Zn reduces WO_3 readily at about $300\text{--}400^\circ$ in air, and a lower oxide W_2O_5 is formed.	12. Zn reduces MoO_3 readily and in air the lower oxide Mo_2O_5 is formed.	
13. WO_3 when heated with powdered Mg is reduced to WO_2 in air, and W_2O_3 in H.	13. MoO_3 when similarly treated, yields Mo_2O_3 if reduced in air, and MoO_2 if reduced in H.	

Causes of the chemical similarity of Wolfram and Iron.

We have commented on the close resemblance which exists between wolfram and iron. Both are hard, difficultly fusible, malleable metals; both file and polish readily. Both undergo cementation when heated with carbon; both are tempered by plunging when hot into cold water. Both form oxides and chlorides, which resemble each other. This chemical and physical similarity should, therefore, arise out of the fact that the atoms of both elements attract the same radicles with equal forces.

Recently*) the heat of combination of oxygen and wolfram has been determined; and the data shows that both iron and W attract O with nearly the same intensity of force:

$$\begin{array}{ll} \frac{1}{2} (\text{Fe}, \text{O}) = 32.3 & \frac{1}{4} (\text{W}, \text{O}^2) = 33.1 \\ \frac{1}{6} (\text{Fe}^2, \text{O}^3) = 32.4 & \frac{1}{6} (\text{W}, \text{O}^3) = 32.74 \end{array}$$

The attraction of Fe for Cl is given by the following numbers:

$$\begin{array}{l} \frac{1}{2} (\text{Fe}, \text{Cl}^2) = 41.00 \\ \frac{1}{3} (\text{Fe}, \text{Cl}^3) = 32.00 \end{array}$$

The corresponding numbers for the heat of formation of the chlorides of W are unknown, but should lie close to the corresponding iron chlorides.

The chemical similarity of iron and wolfram is all the more worth noticing, inasmuch as iron and wolfram are metals which exhibit very different degrees of valence towards the same radicles, eg. the most characteristic oxide of iron is Fe_2O_3 , of W is WO_3 .

In fact, the chemical similarity of elements does not depend at all upon the degree of valence they manifest but solely upon the intensity of the force with which they attract other radicles. (Compare B and Si).

Causes of the chemical similarity of LiCl and SrCl_2 .

The lithium and strontium atoms in general attract the same atoms with nearly the same intensity of force; and in particular they both attract Cl with very nearly the same force, as is shown by the heat evolved when an atom of Cl combines with Li and Sr.

$$(\text{Cl}, \text{Li}) = 93.8 \qquad (\text{Cl}, \text{Sr}^{1/2}) = 92.3.$$

According to the foregoing pages, both compounds should therefore react chemically in a similar manner, and moreover should resemble each other in those physical properties which depend upon the forces which bind the atoms together in the

* Délépine and Halloperm. C. R. (1899). 129. 600—603.

molecule. An examination of their properties shows that this is the case.

LiCl	SrCl ₂	Inferences
1. White crystalline powder; tastes like NaCl.	1. White crystalline powder which a sharp taste.	
2. Melts at a dark red heat to a clear liquid, which gives off Cl and becomes alkaline when heated in air.	2. Melts at 825° C (Carnelly) to a glass like mass with an alkaline reaction.	2. Both bodies seem to have the same degree of fusibility, and the same temp ^o of decomposition.
3. Completely decomposed by heating in steam with the evolution of HCl.	3. Completely decomposed by heating in steam with the evolution of HCl.	3. Chlorine seems to be attached to the Li with about the same intensity of force as it is attached to Sr. Superheated steam has no action, or very little, on NaCl, thus showing that LiCl resembles SrCl ₂ more in this respect than it resembles NaCl.
4. LiCl is easily soluble in water at 0° C solub.=63.7	4. SrCl ₂ is easily soluble in water. Solubility at 0° C = 44.2.	

When it is remembered that SrCl_2 probably possesses a molecule nearly 4 times as heavy as that of LiCl ($\text{SrCl}_2 = 158$, $\text{LiCl} = 42.4$), it will be seen that those properties which depend upon the magnitude of the molecular weight should differ largely in the two compounds; and this is the case.

For example, the

Sp. Gravity of LiCl at 0° is 1.998
" " " SrCl_2 " 0° " 2.96

Evidently solubility in water is not a property which depends upon the magnitude of the molecule, for both substance, comparatively speaking, approach each other closely as regards their solubility.

Strangely enough the melting points of similar compounds does not appear to depend upon the weight of the molecules, but upon their chemical nature because, as a rule, they melt at temps^o which lie close together in spite of great differences in their mol. wgt. For example LiCl and SrCl_2 both melt at a red heat; these salts must possess a molecular attraction, which does not differ very greatly. This is so with chemically similar substances in general, and seems to indicate that it is the internal forces with which the constituent atoms of a molecule are bound together that determines the external force with which the molecules themselves are attracted together.

This explains, why the molecules of chemically similar elements produce corresponding compounds whose molecules are condensed together to the same extent. For example silicon and boron attract the same radicles with the same force, and at the same time their corresponding combinations are each to each, of the same degree of complexity. For instance B_2O_3 and SiO_2 are both complexly polymerised molecules, $(\text{B}_2\text{O}_3)_n$; $(\text{SiO}_2)_n$; whereas SiCl_4 and BCl_3 are both volatile liquids, whose molecular weights correspond to the formula.*)

*) Compare HF and H_2O on p. 86.

Causes of the chemical similarity of NaCl and BaCl₂

Na and Ba are also radicles which in general attract the same atoms with forces which do not differ very greatly and in particular they both attract Cl with the same force, as appears from the thermal data:

$$(\text{Cl, Na}) = 97.7 \qquad (\text{Cl, Ca}^{1/2}) = 97.3.$$

NaCl and BaCl₂ should therefore possess very similar chemical and physical properties. An examination of their properties shows that this is the case:

NaCl	BaCl ₂	Inferences.
1. Melts at 851° (Meyer & Riddle)	1. Melts about 860° (Carnelly).	1. Both bodies seem to possess about the same degree of fusibility.
2. Easily soluble in water. Solubility at 5° = 35.6.	2. Easily soluble in water. Solubility at 5° = 32.2°.	2. Both bodies seem to possess about the same degree of solubility.
3. White crystalline solid with a bitter taste.	3. White crystalline solid with a bitter taste.	
4. Superheated steam has a very slight reaction on NaCl. (Lunge).	4. Heated in steam HCl is evolved and the residue has an alkaline reaction.	4. Cl at a high temp° is attached to the Na with a greater intensity of force than the Cl is attached to the Ba. This is also indicated by the greater H.F. of NaCl.
5. Unchanged by heating in dry O.	5. Unchanged by heating in dry O.	
6. Fusion with KClO ₃ decomposes a trace of NaCl.	6. Partly oxidised by fusion with KClO ₃ ,	6. Cl is attached with a greater intensity of force to the Na than to the Ba.

The mol. wgt corresponding to NaCl is 58.5, and to BaCl₂ is 208 — that is BaCl₂ is nearly 4 times heavier than NaCl.

Here also, then, those properties which depend upon the chemical forces will lie close together and those which depend upon the magnitude of the molecular weight will lie far apart.

Undoubtedly the Sp. Grav. depends largely upon the molecular weight:

Sp. Grav. of NaCl is 2.16

Sp. Grav. of BaCl₂ is 3.79 to 3.89

While the melting points and solubility in water cannot depend largely upon the magnitude of the molecular weight, but must depend upon the chemical forces.

{ NaCl melts at 851°
 { BaCl₂ melts at about 860°

	at 5°	the solubility of NaCl in water is	35.6	}	
	"	"	" BaCl ₂ " " "	32.2	}
at 25—30°	"	"	" NaCl " " "	36.1	}
	"	"	" BaCl ₂ " " "	38.2	}

In this respect the melting points and boiling points of substances differ very widely from such constants as the critical temperatures of gaseous substances, which depend almost entirely upon the magnitude of the molecular weight.

Causes of the chemical similarity of CoCl₂ and NiCl₂.

In the previous cases we have been dealing with compounds, in which, although the chlorine is fixed with the same force in both compounds, yet otherwise they differ not only in the magnitude of their molecular weights, but also in the number of atoms contained in the molecule.

In the case of compounds such as NiCl₂ and CoCl₂ which possess the same molecular weight (CoCl₂ = 130, NiCl₂ = 129) and the same number of atoms in the molecule, and in which in addition the chlorine is attracted by both metals with nearly the same intensity of force, the resemblance in properties becomes remarkable:

CoCl ₂	NiCl ₂	Inferences.
1. [Cl,Co ¹ / ₂] = 38.2	1. [Cl,Ni ¹ / ₂] = 37.2.	1. The chlorine is attached both to the Co and the Ni with nearly the same intensity of force.
2. Heat of solution in water = 18.3	2. Heat of solution in water = 19.3.	
3. Sublimes readily.	3. Sublimes readily.	3. Most chemically similar compounds have nearly the same degree of volatility.
4. CoCl ₂ when heated in steam gives CoO. When a mixture of CoCl ₂ and NH ₄ Cl is heated in a stream of air or O, Co ₃ O ₇ is formed.	4. Heated in air, Cl is evolved and NiO formed. Heated in a stream of O, is entirely changed to Ni ₃ O ₄ .	4. Cl is attached with about the same force both to Co and to Ni.
5. Forms a hydrate CoCl ₂ . 6H ₂ O which slowly loses water over strong H ₂ SO ₄ to form CoCl ₂ . 2H ₂ O.	5. Forms a hydrate CoCl ₂ . 6H ₂ O, which slowly loses H ₂ O over H ₂ SO ₄ to form NiCl ₂ . 2H ₂ O.	CoCl ₂ and NiCl ₂ are capable of exerting external chemical forces of the same intensify.
6. Combines with NH ₄ Cl to form CoCl ₂ . NH ₄ Cl . 6H ₂ O.	6. Combines with NH ₄ Cl to form NiCl ₂ . NH ₄ Cl . 6H ₂ O.	
7. With ammonia forms the compounds: CoCl ₂ . 6NH ₃ CoCl ₂ . 4NH ₃ CoCl ₂ . 2NH ₃	7. With ammonia forms the compounds: NiCl ₂ . 6NH ₃ — — NiCl ₂ . 2NH ₃	

Causes of the chemical similarity of ICl_3 and ICl .

ICl and ICl_3 are chemically similar substances because at ordinary temperatures *) the force which attracts the chlorine to the iodine in both substances does not differ greatly and is very feeble, as is shown by the thermal data:

$$(\text{I}, \text{Cl}) = 6.7 \qquad \frac{1}{3} (\text{I}, \text{Cl}^3) = 7.2$$

So that we should expect that those influences which will part the chlorine from the one, will also part the chlorine from the other compound. The two compounds should therefore react chemically in the same way.

And this is in general the case. We contrast the properties of the two compounds:

ICl	ICl_3	Inferences.
1. Brown oily liquid, which on standing passes into a red-dish solid.	1. Yellow red solid.	
2. Very volatile; its vapour density has been determined at 120° .	2. Very volatile, easily subliming.	2. Both compounds approach each other as regards volatility.
3. Smells of I and Cl , and attacks all mucous membranes rapidly and forms very bad sores if let fall on the skin.	3. Very disagreeable smell, attacks nose and eyes.	3. The external chemical affinities of both substances are very much the same.
4. Water decomposes ICl forming HCl and HIO_3 and I .	4. Water decomposes ICl_3 forming ICl , HCl and HIO_3 .	} The chlorine and I seems to be attracted together

*) ICl_3 varies very rapidly in stability. Below 0° it is more stable than ICl , and above 20° it is less stable. At some intermediate temperature its equivalent heat of formation equals that of ICl .

ICl	ICl ₃	Inferences
5. KOH soln. produces KIO ₃ , KCl and KI with separation of I.	5. KOH produces KCl and KI, KClO ₃ and KIO ₃ .	} with about the same force in each compound, since the same reagent are capable of simultaneously decomposing both bodies
6. NH ₃ soln. forms NH ₄ Cl and NI ₃ , wh. combines with a portion of the NH ₃ .	6. NH ₃ soln. produces NH ₄ Cl, NH ₄ I and NI ₃ .	

It will be seen that these two compounds, in spite of very dissimilar formulae, and molecular weights of very different magnitudes ($\text{ICl} = 162.5$, $\text{ICl}_3 = 233.5$) react in very much the same way both chemically and physically because it happens that the chlorine is attached to the I atom with nearly the same force in each; and that in addition both compounds are formed out of the same materials (viz. Cl and I). The sole condition that two bodies should be formed out of the same materials is, of course, not sufficient to determine chemical similarity; the atoms must at the same time be bound together with the same force. For example, PbCl_2 acts in quite a different way to PbCl_4 , because although both are formed out of the same material, the chlorine is attached with two different forces to the Pb in these two different compounds.

ICl and ICl_3 illustrate how greatly the volatility of compounds depends upon the force with which the atoms are bound together in the molecule and how little upon the mere magnitude of the molecular weight.

Causes of the chemical similarity of CaO, BaO, SrO.

CaO = 56	SrO = 103	BaO = 153.	Remarks.
1. S.G. 3.15	1. S.G. 4.7.	1. S.G. 5.7.	1. The specific gravity seems to depend largely upon the magnitude of the

CaO = 56	SrO = 103	BaO = 153	Remarks
			molecule, and not upon the chemical forces.
2. Slightly soluble in water. $S_0^0 = 1.3$	2. Slightly soluble in water. $S_0^0 = 0.90$.	2. Slightly soluble in water. $S_0^0 = 1.5$.	2. Solubility seems to be almost independent of the magnitude of the molecules, but depends largely upon the nature of the molecule.
3. White amorphous powder.	3. A grey-white porous solid.	3. A grey-white powder.	
4. Infusible at a white heat.	4. Infusible at a white heat; but melts in the electric furnace (C. 3000°).	4. Liquefies at about 2000°.	4. All bodies are characterised by their intense infusibility and involatility. CaO with the lightest molecule being the most infusible and most stable. BaO, the heaviest, the most fusible and most unstable.
5. Unchanged at 1750° (Read) Not decomposed in electric furnace. (Moissan).	5. Unchanged at 1750° (Read) Not decomposed at 3000° (Moissan).	5. Unchanged at 1750° (Read). Not decomposed at 2500° (Moissan).	5. All bodies are characterised by the intense force with which the O is attached to the metal. So that even the most intense temps°

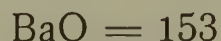
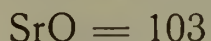
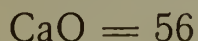
CaO = 56	SrO = 103	BaO = 153	Remarks
			are not able to decompose these bodies.
6. Strongly basic, reacting with water to form an intensely caustic hydroxide.	6. Strongly basic, reacting with water to form an intensely caustic hydroxide.	6. Strongly basic, reacting with water to form an intensely caustic hydroxide.	The atoms in the molecule of all these oxides seem to be held together by chemical forces of the same intensity, inasmuch as they undergo the same reactions when exposed to the same influences.
7. React with most acids to form salts.	7. Reacts with most acids to form salts.	7. Reacts with most acids to form salts.	
8. Heated in chlorine CaCl_2 is formed.	8. —	8. Heated in chlorine BaCl_2 and O are formed.	
9. Decomposed by heating with K	9. —	9. Decomposed by heating with K.	
10. Heat of formation is $\frac{1}{2}[\text{Ca}, \text{O}] = 65$	10. $\frac{1}{2}[\text{Sr}, \text{O}] = 64$	10. $\frac{1}{2}[\text{Ba}, \text{O}] = 62$	10. The atoms in the molecules of all these oxides seem to be attracted together with nearly the same intensity of force.

Notice:

- a) That the heats of formation approach each other closely. —
 That is the atoms are attracted together in the molecules with nearly the same intensity of force:

$$\frac{1}{2}(\text{Ca}, \text{O}) = 66 \quad \frac{1}{2}(\text{Sr}, \text{O}) = 64 \quad \frac{1}{2}(\text{Ba}, \text{O}) = 62$$

- b) That they all approach each other as regards fusibility and volatility. All are difficultly fusible and insoluble solids and this in spite of very different mol. wts.



Again showing that the fusibility and volatility of solids depends to a much greater degree upon equality of chemical forces than upon the magnitude of the molecular weights.

Volatility, fusibility, solubility.

Bodies which react in a very similar way with different reagents usually approach each other closely as regards volatility.

Chemically similar compounds almost invariably possess nearly the same degree of volatility, though they often differ very widely indeed as regards the magnitude of their molecular weights. It is, in fact, not those compounds which approach each other most closely in the way which they react chemically which approach each other most closely in the magnitude of their molecular weights. Rather it is those compounds (and also elements) which resemble each other most closely in the way they react chemically which approach each other most closely as regards volatility.

We have already met with many illustrations of this fact in the preceding pages. We add here a few new illustrations.

Thiophene derivatives.

The thiophene derivatives are known to exhibit the greatest chemical similarity to those of Benzene. The replacement of the group C_2H_2 in benzene by sulphur changes its properties so little, that the preparation and properties of the thiophene derivatives in part agree almost word for word with these of benzene*) That these chemically similar bodies also possess nearly the same

*) van't Hoff. Lectures III. 143.

degree of volatility appears from the following table (taken from Richter's Organic Chemistry. Vol. II [1900] p. 453):

Benzene Series.	B. Pt.	Thiophene Series.	B.Pt.
Benzene	80.5 °	Thiophene	84 °
Toluene	110.3 °	Thiotolene	113 °
p. Xylene	138 °	1, 4-thioxene	135 °
Isopropyl benzene . .	153 °	Isopropyl thiophene .	154 °
Diphenyl	254 °	Dithiënyl	266 °
Diphenyl methane . .	261 °	Dithiënyl methane . .	267 °
Chlorbenzene	132 °	α -chlorthiophene . . .	130 °
p. dichlorbenzene . .	172 °	Dichlorthiophene . .	170 °
Brombenzene	155 °	α -Bromthiophene . .	150 °
Tetra-brombenzene .	329 °	Tetrabromthiophene .	326 °
p. dinitro-benzene . .	299 °	Dinitrothiophene . .	290 °
Benzoic acid	250 °	α -thiophene carboxylic acid	260 °
Benzo-nitrile	191 °	Thiophen-nitrile . . .	190 °
Acetophenone	202 °	Acetothiënare	213 °
Benzophenone	307 °	Thiënone	326 °
Cinnamic acid . m. pt.	133 °	Thiënyl acrylic acid m. pt.	138 °

ICl and IBr.

ICl and IBr exhibit a remarkable resemblance to each other in their chemical behaviour.

Also both compounds approach each other closely as regards volatility, each giving off a perceptible amount of vapour at ordinary temperatures, and each can be easily sublimed at temperatures a little above 100 °. In spite of this they differ widely as regards the magnitude of their molecular weights (162 and 207).

SeCl₄ and SeBr₄.

These bodies also resemble each other very closely as regards the way they react. Although they differ very widely as regards the magnitude of their molecular weights (220 and 390) yet both possess nearly the same degree of volatility, both volatilising below 100 ° without melting.

Similarly Se_2Cl_2 and Se_2Br_2 are chemically similar. Both substances are at ordinary temperatures liquids although they differ widely as regards the magnitude of their molecules (228 and 318).

Did the volatility of compounds depend to any great extent upon the magnitude of the molecule, we should have expected such compounds of selenium to be characterised by their fixity rather than by their volatility.

UCl_4 and UBr_4 .

Uranium possesses one of the heaviest atoms known. Its compounds should therefore be characterised by their fixity, did the volatility of compounds depend largely upon the weight of the molecules. Instead of this being the case their halogen compounds are characterised by their volatility. UCl_4 and UBr_4 possess very heavy molecules which differ widely in magnitude ($\text{UCl}_4 = 380$, $\text{UBr}_4 = 558$).

In spite of this fact:

1. Both compounds react in nearly the same way chemically.
2. At the same time have nearly the same degree of volatility (both volatilise at a low red heat).

RuO_4 and OsO_4 .

Both the compounds react in a very similar way chemically. They also resemble each other closely in respect to their volatility; in fact both compounds are characterised by their surprising volatility. (Both volatilise with ease at the boiling point of water.) Yet they differ very widely as regards the magnitude of their molecules. ($\text{RuO}_4 = 164$, $\text{OsO}_4 = 255$.)

HCl and HBr .

HCl and HBr react in the same way chemically. Both possess nearly the same degree of volatility. For example both are volatile enough to be gaseous at ordinary temps⁰. HCl boils at -83.7° , HBr at -64.9° ; so that by increasing the temp⁰ by a small range of 19° , we convert both into the gaseous condition, and this although the molecule of HBr is more than twice as heavy as the molecule of HCl . (81 : 36.5).

Notice that both are characterised by their great solubility in water. Chemically similar bodies always possess closely allied degrees of solubility.

BCl_3 and SiCl_4 .

React in the same way chemically. Also both possess nearly the same degree of volatility and fusibility. For example, both are fusible enough to be in a liquid condition at ordinary temperatures and both are converted into the gaseous condition within a range of temperature of less than 40°C .

(BCl_3 boils at 18° , SiCl_4 at 57.5° .)

à priori there is nothing to prevent BCl_3 boiling at 18° and SiCl_4 at 500° .

The mol. wgt. of BCl_3 is 117, of SiCl_4 is 169.7.

We have taken these particular cases at random. A general review of the elements and their compounds will convince one of the truth of the observation that those elements and compounds which approach each other most closely as regards their chemical behaviour are also those which approach each other most closely as regards their volatility; and the more widely do the elements or compounds differ as regards their chemical behaviour the more widely do they differ as regards volatility.

To perceive this relationship we have only to think of the corresponding degrees of volatility of the compounds of the halogens, Cl, Br, I, of the sulphur elements (S, Se, Te), of the alkali elements (Li, Na, K, Rb, Cs) &c.

It must be remembered that all grades of volatility, from that of a perfect gas to that of an infusible solid are possible to the compounds of any given element.

And *à priori* there is no particular reason why bodies which react in the same way towards reagents should possess the same degree of volatility. It can with be imagined that two compounds which are chemically similar — that is to say react in the same way — should differ very widely as regards their volatility, especially as many such compounds differ enormously as regards the magnitude of their molecular weights. This, however, is never the case.

Inference.

These facts lead one to believe, that the volatility of compounds is determined to a very much greater extent by the factors which cause the chemical similarity of compounds than by the magnitude of their molecular weight.

But the factors which determine the chemical similarity of compounds are as we have seen the intensities of the forces which bind together the atoms in the molecule.

Consequently we infer that the volatility of compounds is determined almost entirely by the intensity of the forces which bind together the atoms in the molecule.

Influence of the molecular weight.

The magnitude of the molecular weight is a factor of only secondary importance as compared with the chemical forces in determining the volatility of a compound.

In the interior of a liquid a molecule is subject to an intense attraction from other molecules, but this attraction is exerted equally in all directions and so has no directive influence on the motion of the molecule.

At the surface of a liquid, however, the molecule is not attracted equally in all directions, but is pulled backwards into the interior of the liquid by the attractive force of the molecules from below. A molecule, therefore, in motion towards the surface has its motion diminished or even reversed by this attractive force and so may fail altogether to break away from the liquid and continue its motion as vapour outside.

And obviously the greater the magnitude of this attractive force, the smaller will be the number of molecules which will succeed in thus escaping, and thus the smaller the volatility of the liquid.

The volatility of a substance, then, depends essentially upon the force with which neighbouring molecules are attracted together.

Now the force with which neighbouring molecules attract each other depends upon two factors:

1. Upon the total quantity of matter in the molecule and upon the molecular weight. In general the greater the the molecular weight the greater the molecular attraction, and consequently the smaller the volatility of the substance.
2. Upon the chemical forces binding together the atoms in the molecule.

It is a prevalent idea that the magnitude of the molecular weight is the factor of greatest moment in determining the volatility of compounds.

The whole of Henri's paper **Phil. Mag.** (1885) [5]. 20. 81. is based on this conception. He endeavours to prove that the greater volatility of chlorides over oxides arises from the molecular condensation of the latter. The same line of argument would prove that the greater volatility of non-metals over metals is caused by the greater complexity of the molecules of the latter. As a matter of fact the molecules of metals are less complex than the molecules of non-metals, and the greater fixity of the former bodies arises not from their greater molecular weight, but from the fact that the molecules of metals attract each other more strongly than molecules of non-metals.

We will show, however, by means of the following and preceding researches, that as a matter of fact, this factor is of quite subordinate importance as compared with the chemical forces in determining the volatility. So much so that the former influence only becomes visible when one eliminates the effect of the latter by dealing with chemically similar substances — that is to say, substances the intensity of whose chemical forces is the same. It thus happens that there exists substances composed out of light molecules which are very much less volatile than substances composed out of heavy molecules because the light molecules attract each other more strongly than the heavy molecules do, in precisely the same way that some elements attract each other more strongly than they do others, and this quite

independently of the magnitude of their atoms: For example F and O have not the slightest chemical attraction for each other: F and H however combine explosively; and this in spite of the fact that the O atom is 16 times heavier than the H atom.

Was the volatility of compounds quite independent of the chemical forces and depended only upon the magnitude of the molecules, then two results would be inevitable:

1. All chemical substances which have the same molecular weight would have the same degree of volatility.
2. The compounds which have the heavier molecules would have the smaller degree of volatility.

These conclusion are not correct and so the assumptions on which they are founded cannot be correct. We will now proceed to illustrate how sometimes the lightest molecules are the less volatile.

The molecule of OsO_4 is 11 times heavier than the sodium molecule ($\text{OsO}_4 : \text{Na} :: 255 : 23$) and yet is enormously more volatile. Na is gaseous at a bright red heat (900°); OsO_4 at the boiling point of water.

Xenon with a molecular weight of 125 is so volatile as to be gaseous at ordinary temperatures; whereas methyl alcohol CH_3OH with a molecular weight of 32 is liquid at ordinary temperatures.

The Xenon molecule is 4 times heavier than the alcohol molecule and yet is enormously more volatile.

UBr_4 with a molecular weight of 558 is enormously more volatile than CrCl_2 with a molecular weight of 123. The first assumes the gaseous condition at a red heat; the second at a white heat. The vapour densities correspond to these molecular weights. UBr_4 forms one of the heaviest vapours known; its molecule is more than $4\frac{1}{2}$ times heavier than that of CrCl_2 .

$\text{Ni}(\text{Co})_4$ with a molecular weight of 170 boils at 43° (760)
Hexane (normal) with a molecular weight of 86 boils at 71° C.

The one molecule is twice as heavy as the other, and yet is more volatile.

Helium (mol. wgt. 4) is more volatile than hydrogen (mol. wgt. 2). Uranium (mol. wgt. 240) is much more volatile than iron (mol. wgt. 56).*)

Fluorine (mol. wgt. 38) is more volatile than oxygen (mol. wgt. 32).**) Fluorine boils at -185° , oxygen at -183° .

Mercury with a mol. wgt. of 200 boils at 349°

Cadmium " " " " 112 " " 763°

Zinc " " " " 65 " " 950°

Magnesium " " " " 24 " " 1100°

The volatility of the metals is inversely as the molecular weight. The Hg molecule weighs more than 8 times the magnesium molecule and yet is enormously more volatile:

The volatility of the three metals Ag, Cu, Au, follows the order of their valencies and not the order of their atomic weights.***)

Ag is much more volatile than Cu, though their molecules stand in the ratio 198 : 63. In a vacuum Ag boils about 1400° C, copper between 1500° and 1000° .

SF_6 is enormously more volatile than S_2Cl_2 , though their molecules do not differ greatly in magnitude ($\text{SF}_6 = 146$, $\text{S}_2\text{Cl}_2 = 135$). The one is a volatile gas (B.Pt -55°), the other a liquid which boils at $+138^{\circ}$.

SF_6 is more volatile than chlorine gas (B. Pt -34°), though the molecule of the former is twice as heavy as that of the latter (145 : 71).

SCl_4 with a mol. wgt. of 174 is more volatile than S_2Cl_2 which has a mol. wgt. of 135.

The same is true of Se_2Cl_2 and SeCl_4 . (Mol. wgt 228 and 220).

ClO_2 with mol. wgt. of 67.5 boils at $+9^{\circ}$

Cl_2O " " " " 87 " " -17°

*) Moissan Comp. Rend. (1896). 122. 1088—1093.

**) Moissan and Dewar. Comp. Rend. (1897). 1202—1205.

***) Krafft. Ber. (1903) 36. 1090.

SF_6 boils at -55° ; SO_2F_2 boils at -52° ; SOF_2 at -32° .*

So that SF_6 with a mol. wgt, at 146 is more volatile than SO_2F_2 with a mol. wgt. of 102, and this is more volatile than SOF_2 with a mol. wgt. of 86.

The volatility is inversely as the molecular weight.

UCl_5 is more volatile than UCl_4 , though as shown by their vapour densities, the molecular weights stand in the ratio 417:382.

InCl_3 (mol. wgt. 219.5) is more volatile than InCl_2 (mol. wgt. 184); and this is more volatile than InCl (mol. wgt. 148.5).

GaCl_3 with a mol. wgt. of 175.5 is more volatile than GaCl_2 with a mol. wgt. of 140.

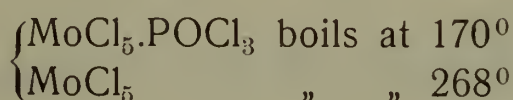
FeCl_3 with a mol. wgt. of 162.5 more volatile than FeCl_2 with a mol. wgt. of 127.

CoCl_3 with a mol. wgt. of 158.5 is more volatile than CoCl_2 with a mol. wgt. of 123.

All these chlorides have been gasified and their molecular weight determined.**

$\text{MoO}_3 \cdot 2\text{HCl}$ is very much more volatile than MoO_3 . The one sublimes below 150° , the other at a red heat.

$\text{MoO}_3 \cdot 2\text{HCl}$ has the mol. wgt. 217,*** MoO_3 the mol. wgt. 144.



Yet (as shown by their vapour densities) the molecule of MoCl_5 weighs 272.5, and the molecule of $\text{MoCl}_5 \cdot \text{POCl}_3$ not less than 426.

Smith and Oberhaltzen (Zeit. Anorg. Chem. [5]. 63.) describe a compound of W, S and Cl, of formula $\text{W}_2\text{S}_4\text{U}_8$, which is quite volatile at a red heat.

Here, then, is a compound which possesses the enormous molecular weight of 876 and yet is characterised by its volatility! Did the volatility of bodies depend to any great extent upon the magnitude of the molecule, this body should be characterised by its fixity.

*) Moissan C. R. (1900). 130. 805—871.

**) Nilson and Petterssen. J. C. S. (1888). 53., 812.

***) Vandenberghe. Zeit. Anorg. Chem. (1895). 10. 47—59.

The iodide of an element is usually more fusible and volatile than the bromide, and this than the chloride, which the flouride is the most infusible and involatile.*)

Thus AgI volatilises more readily than either AgBr or AgCl.**)

Henri***) shows that sometimes the replacing of hydrogen by fluorine causes an increase in volatility notwithstanding that the molecular weights are increased;

$\begin{cases} \text{CHCl}_3 \text{ boils at } 61^\circ \\ \text{CFCl}_3 \text{ „ „ } 24^\circ \end{cases}$	$\begin{cases} \text{CH}_2\text{Cl}_2 \text{ boils at } 41^\circ \\ \text{CHFCl}_2 \text{ „ „ } 14.5^\circ \end{cases}$
$\begin{cases} \text{CH}_2\text{Cl.Br} \text{ boils at } 68^\circ \\ \text{CH.F.Cl.Br} \text{ „ „ } 38^\circ \end{cases}$	$\begin{cases} \text{CHCl}_2.\text{COCl} \text{ boils at } 107^\circ \\ \text{CFCl}_2.\text{COCl} \text{ „ „ } 75^\circ \end{cases}$
$\begin{cases} \text{CHCl}_2.\text{COOH} \text{ boils at } 190^\circ \\ \text{CFCl}_2.\text{COOH} \text{ „ at } 102.5^\circ \end{cases}$	$\begin{cases} \text{CHCl}_2.\text{COOEt} \text{ boils at } 157^\circ \text{ C} \\ \text{CFCl}_2.\text{COOEt} \text{ „ „ } 130^\circ \end{cases}$
$\begin{cases} \text{CHCl}_2.\text{CONH}_2 \text{ boils at } 233^\circ \\ \text{CFCl}_2.\text{CONH}_2 \text{ „ „ } 215^\circ \end{cases}$	$\begin{cases} \text{CH}_3.\text{COH} \text{ boils at } 21^\circ \\ \text{CH}_3.\text{COF} \text{ „ „ } 20.8^\circ \end{cases}$
$\begin{cases} \text{C}_2\text{H}_5.\text{COH} \text{ boils at } 49^\circ \\ \text{C}_2\text{H}_5.\text{COF} \text{ „ „ } 44^\circ \end{cases}$	$\begin{cases} \text{C}_5\text{H}_6.\text{COH} \text{ boils at } 179^\circ \\ \text{C}_5\text{H}_6.\text{COF} \text{ „ „ } 154^\circ \end{cases}$

Also cases are known where the introduction of chlorine instead of hydrogen causes an increase of volatility:

NC.CH ₂ Cl	boils at	123°
NC.CHCl ₂	„ „	112°
NC.CCl ₃	„ „	83°

Here the volatility increases as the molecular weight increases.

Isomeric compounds have different degrees of volatility, although they have the same molecular weights.

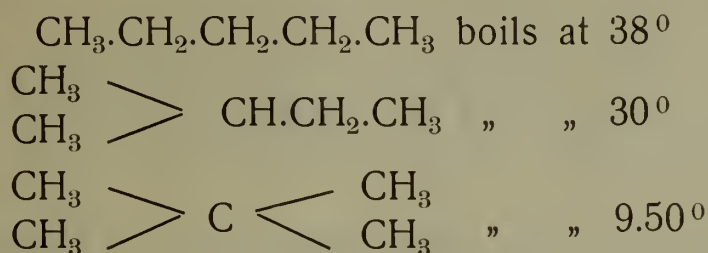
In the fatty series, the normal compound has the highest boiling point. The more the chain of carbon atoms assumes a

*) Lothar Meyer. "Outlines" p. 119. (1899).

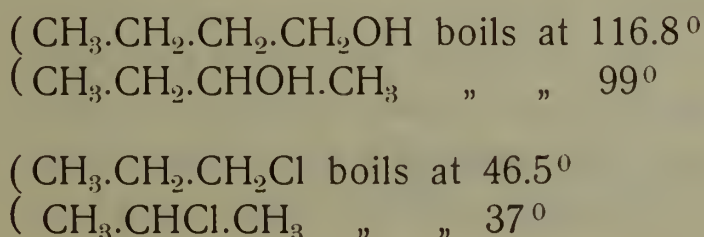
**) Clowes and Coleman. Quantitative Analysis. p. 99. (3. edition 1895).

***) Rect. Trav. chim. (1897) 16. 218—225.

branching type — that is, the more "spherical" the molecule becomes, the more volatile is the body.*)



If the isomers contain O or Cl, the volatility increases as O or Cl atoms approach the centre of the molecule:



In the case of isomers of the Benzene series, ortho-compounds boil at higher temperatures than the meta-compounds, and these in turn about the same or a higher temperature than the para-compounds.

Thus, of the 3 dichlorobenzenes, the ortho-compound boils at 179° , the meta- at 172° and the para- at 172° .

In all these cases the comparatively slight change in the intensity of the chemical forces at play within the molecule, produced by an alteration of the spacial arrangement of the atoms, is thus quite sufficient to cause large fluctuations in the volatility, although the molecular weight and the atoms themselves remain unchanged.

It will thus be seen that the chemical forces are a factor of greater influence in determining volatility than the magnitude of the molecular weight.

It is, in fact, only when we eliminate the effect of the chemical forces by considering chemically similar compounds — that is to say, compounds the atoms of whose mole-

*) Nernst Theo. Chem. p. 280.

cules are bound together with chemical forces of the same intensity — that the effect of the molecular weight becomes in any degree visible.

For example the following are all in ascending order as regards molecular weight and in descending order as regards volatility:

CO and CO₂; NO and NO₂; As₂O₃ and As₂O₅; P₂O₃ and P₂O₅;
HCl, HBr, HI; AlCl₃, GaCl₃, InCl₃ O, S, Se, Te;
F, Cl, Br, I; He, Ne, Ar, Kr, Xe.

The homologous alcohols, acids, hydrocarbons &c.

But even with chemically analogous compounds exceptions occur; for example UCl₅ is more volatile than UCl₄; FeCl₃ than FeCl₂; InCl₃ than InCl₂, and InCl₂ than InCl; GaCl₃ than GaCl₂; Cl₂O than ClO₂; HCl than HF &c. &c.

Influence of Valence.

The foregoing researches bring to light a remarkable connection between the valency of an element and the volatility of the compounds it gives rise to.

The compounds of high valency grade are almost invariably more volatile than compounds of a low valence grade, in spite of the fact that their molecules are heavier.

The higher the grade of valence the more characteristic becomes the volatility.

In this connection we may recall to mind the conspicuous volatility of such compounds as Ni(CO)₄; OsO₄; RuO₄; Mn₂O₇; which are all remarkable both by reason of their great volatility, and because they are the highest types of combination known.

We will briefly recapitulate the chief facts bearing on the matter:

SbCl₅ is more volatile than SbCl₃;

UCl₅ is more volatile than UCl₄, and UCl₄ more volatile than the lower chlorides.

WCl_6 and WCl_5 are more volatile than WCl_4 and this more volatile than the still lower chlorides.

FeCl_3 is more volatile than FeCl_2 ; InCl_3 than InCl_2 ; InCl_2 than InCl ; GaCl_3 than GaCl_2 and GaCl_2 than GaCl .

CrCl_3 is more volatile than CrCl_2 ;

CrO_3 is more volatile than any of the lower oxides of Cr

MoO_3 " " " " " " " " " " Mo

WO_3 " " " " " " " " " " W

UO_3 " " " " " " " " " " U

Mn_2O_7 is a liquid, whereas all the lower oxides are involatile solids.

NO_3 is a liquid which does not freeze in a mixture of ice and salt. (Berthelot). N_2O_5 is a solid.

OsO_4 is more volatile than any of the lower oxides of Os (which are all involatile and infusible). RuO_4 is more volatile than any of the lower oxides of Ru (which are all involatile and infusible).

SF_6 is more volatile than SOF_2 . The one contains hexavalent sulphur, the other tetravalent.

All the high-grade compounds of Cr, W, Mo, U, Va &c. are characterised by their volatility. The tendency is particularly manifest in the multitude of high grade oxy-halides they produce.

The lower grade compounds of the same type are all much less volatile.

SeBr_4 is more volatile than Se_2Br_2 , although it has a heavier molecule. ($\text{SeBr}_4 = 399$, $\text{Se}_2\text{Br}_2 = 320$).

Two points call for attention :

- In metallic compounds the rule is almost invariably obeyed. The influence of valence has a very much greater influence on the volatility than the increase of atomic weight.
- In non-metallic compounds the rule is sometimes obeyed, something not — the molecular weight here exerting a great influence.

For example SO_2 is more volatile than SO_3 , but SO_3 is less volatile than S_2O_7 .

SF_6 is more volatile than SOF_2 .

NO_2 is more volatile than N_2O_5 , but N_2O_5 is less volatile than NO_3 .

It will be remembered that in organic chemistry it is a well known generalisation that unsaturated compounds are less volatile than saturated compounds of the same molecular magnitude.

It thus appears that the higher the grade of valence the less the intensity of the force with which the molecules attracts each other.

High grade compounds are usually unstable, and it might be thought that this is the reason of their greater volatility. (See next article.)

Chemically unstable bodies are usually characterised by their volatility and fusibility; chemically stable compounds by their involatility and infusibility.

The following data illustrates this statement:

SiO_2 is fixed and very stable; SiCl_4 is volatile and easily decomposed.

B_2O_3 is stable and involatile; BCl_3 is easily decomposed and volatile.

Al_2O_3 is stable and involatile; AlCl_3 is volatile and easily decomposed.

SnO_2 is stable and involatile; SnCl_4 is volatile and easy to decompose.

In fact the metallic chlorides generally are more volatile and fusible than the corresponding oxides, and at the same time usually less stable.

AgI is less stable than either AgBr or AgCl ; it is also more volatile. This also is a general rule.

Ni(CO)_4 and Fe(CO)_5 are the most volatile compounds of Ni and Fe known. Yet both are very easy to decompose.

Of all the oxides of uranium, UO_3 is the most volatile and the easiest to decompose by heat.

Similarly the most volatile and at the same time most unstable oxides of Mo and W are MoO_3 and WO_3 .

CrO_3 is more volatile and easier to decompose than CrO_2 ; CrO_2 is more volatile and easier to decompose than Cr_2O_3 or CrO .

The most fusible and also the most unstable oxide of Mn is Mn_2O_7 . Mn_2O_7 , in fact, is at ordinary temperatures a liquid, whereas MnO_3 , MnO_2 , Mn_3O_4 , Mn_2O_3 and MnO are all infusible solids.

OsO_4 and RuO_4 are the most volatile and also the most unstable oxides of Os and Ru. Both sublime easily at 100° ; the other oxides are stable and involatile.

OsO_4 is less volatile than RuO_4 and at the same time more stable.

MoO_3 is more volatile and fusible than WO_3 and at the same time less stable.

CrO_3 is less volatile and more stable than CrO_2Cl_2 , although CrO_3 has the lightest molecule.

UCl_5 is more volatile and easier to decompose by heat than UCl_4 .

WCl_6 is much more volatile and easier to decompose than WCl_4 ; WCl_6 melts at 275° and boils at 347° and decomposes about 440° . WCl_4 , however has not been fused or volatilised.

WO_3 only sublims at a white heat and is not decomposed at the melting point of platinum; WCl_6 is therefore more volatile and unstable than WO_3 .

MoCl_5 is more volatile and easier to decompose than MoCl_4 ; and MoCl_4 is more volatile and easier to decompose than MoCl_3 ; the least volatile and the most stable under the action of heat of all these chlorides is MoCl_2 .

$\text{MoO}_3 \cdot 2\text{HCl}$ is more volatile and more unstable than MoO_3 . The one decomposes at 158° , the other at a white heat.

Similarly $\text{MoO}_3 \cdot \text{PCl}_5$ is more volatile and more unstable than MoO_3 .

MoBr_4 is more volatile and easier to decompose by heat than MoBr_3 ; and MoBr_3 is more volatile and easier to decompose than MoBr_2 .

So that of all the bromides of Mo, MoBr_4 is the most volatile and the same time the most unstable; MoBr_2 the least volatile and the most stable.

FeCl_3 is more volatile and easier to decompose by heat than FeCl_2 .

CrCl_3 is similarly more volatile and less stable than CrCl_2 .

InCl_3 is more volatile and easier to decompose by heat than InCl_2 ; and InCl_2 is more volatile and easier to decompose than InCl .

InCl_2 is less stable and more volatile than GaCl_2 . GaCl_3 is a solid, SbCl_5 is a liquid which easily volatilises, decomposing into SbCl_3 and Cl_2 .

Of all the chloride of the iron group of elements (Al, Fe, Mn, Cr, Ga, In, Tl). CrCl_2 is the least volatile and also the most stable under the action of heat.

The compounds of Mercury can be all easily volatilised, and at the same time can be all easily decomposed by heat.

The Ammonium compounds can be all easily volatilised, and at the same time easily decomposed by heat.

The corresponding compounds of Na and K can neither be volatilised nor decomposed by heat in this way.

MgO , CaO , SrO and BaO are characterised by their great stability and their great involatility.

BN is involatile and stable; C_2N_2 is volatile and unstable.

ICl , IBr , ICl_3 , IBr_3 , Se_2Cl_2 , Se_2Br_2 , SeCl_4 , SeBr_4 , S_2Cl_2 , SCl_4 , &c. &c. are all volatile bodies and at the same time easily decomposed.

HF is very much more stable than either HCl , HBr or HI ; it is also much less volatile, being a liquid at ordinary temperatures whereas the others are gases.

The oxides of chlorine and nitrogen are all characterised by their instability and their volatility.

The order of volatility of the oxides of chlorine follow the order of stability, and not the order of their molecular weight:

Cl_2O	with a mol. wgt. of	87	boils at	-17°	(760 mm)
ClO_2	" " " " "	67.5	" " "	$+9^\circ$	
Cl_2O_7	" " " " "	182	" " "	$+82^\circ$	

Also Cl_2O is less stable than ClO_2 , and ClO_2 is less stable than Cl_2O_7 , which is in fact the most stable and also the most involatile of the oxides of Cl.

The vast majority of known compounds of carbon are either fluids at ordinary temperatures, or become so within a range of 150° .

Indeed it is this fusibility and volatility of the carbon compounds that is their more striking characteristic.

They are also extremely unstable under the action of heat.

Out of the innumerable multitude of carbon compounds capable of existing at ordinary temperatures, not one, perhaps, in 100,000 is capable of existing at a white heat. The domain of organic chemistry is entirely destroyed at a red heat.

Similar remarks apply to the nitrogen compounds; they too are characterised by their volatility and the ease with which they decompose under the influence of heat.

On the other hand the silicates, borates and phosphates, are all characterised by their involatility and their stability.

Inference.

From these facts we conclude that there is a connection between the intensity of force with which the atoms are bound together in the molecule and the volatility of the compound — the connection revealing itself statistically in the fact that the more strongly attracted together are the atoms in the molecule (and therefore the more stable the molecule), the more strongly attracted together are the molecules themselves, and consequently the more involatile the compound.

Conclusion.

It is claimed that in the preceding pages the fact has been established that not only the chemical but also the physical behaviour of elements and compounds are determined almost entirely by the attractional forces which the constituent atoms exert on other molecular and atomic species, and that consequently any method of representing these forces graphically will at the same time represent graphically all the chemical and physical properties of the atom.



Chapter III.

Bearing of the preceding facts on the theory of solution.

Introductionary remarks.

We have come to the conclusion in the preceding pages:

1. That the solubility is determined almost entirely by the external attractive forces the molecules exert, and only to an inappreciable extent by the magnitude of the molecular weight.
2. That the more nearly equal are the external forces, each to each, which two different kinds of molecules or atoms exert on other kinds of atoms or radicles, the more alike chemically and physically are the two kinds of molecules.

We now proceed to consider what light these conclusions throw on the phenomenon of solution.

It has long been known as an empirical fact that chemically similar substances are mutually miscible in all proportions, whereas very dissimilar substances do not mix together.

From (1) we conclude that the difference in solubility is due to the difference of the forces which chemically similar and dissimilar molecules exert.

From (2) we conclude that the immediate cause of the complete mutual solubility of chemically alike substances is due to the fact that their molecules exert forces of the same intensity; and that the immediate cause of the immiscibility of chemically

unlike substances is due to the fact that their molecules exert forces of different intensities. This seems a very important conclusion, and as we proceed to show, throws unexpected light on the phenomenon of solution.

Sphere of molecular activity.

Consider any one molecule, M , inside a fluid. It is surrounded by a group of molecules, and if we take all those molecules which lie within a sphere of extremely small radius whose centre is M , there is a special action exerted on M by each molecule within the sphere, those molecules nearest to M exerting a more powerful action than those near the surface of the sphere.

Beyond a certain distance, E , from M , these special actions are assumed to be insensible; this length E is the radius of the aforesaid sphere, called the sphere of molecular activity.

E is an arbitrary distance, which decreases as we increase the motion of the molecules. For the molecules of a fluid are in incessant motion, and in consequence of this motion are in a state of incessant flux to and fro about every point in the liquid.

So that every molecule remains on an average under the influence of another for a short time t as they pass each other in the liquid. t depends on the velocity of the molecules, and the greater the velocity of the molecule the smaller is t .

If now in the time t during which the molecule A is under the influence of the molecule B , the distance E which separates them is so long that the force which A exerts has in this time no appreciable influence in curving the path of B , we assume that the distance E is the required limit.

If now the velocity of the molecule be increased, the average time t during which one molecule is under the action of another will diminish. And therefore in order that the force which the one molecule exerts on the other may produce an appreciable effect in this shorter time, the molecules must now approach each other closer than previously, for this will make the attractive forces stronger, and so will neutralise the smaller time for which the forces act.

It is clear, therefore, that E decreases as the velocities of the molecules increase; that is E decreases with the temperature.

It is owing to this fact (as we shall see later) that the solubility increases with the temperature and decreases with fall of temperature.

Disturbance of the symmetrical structure of a liquid by the presence of dissolved molecules.

Consider now a liquid whose molecules are all of the same kind. Then the molecules will on the average be arranged symmetrically about every point within it.

If, however, we introduce into the liquid a foreign molecule the foreign molecule will form a centre of disturbance in the liquid and destroy its symmetrical structure.

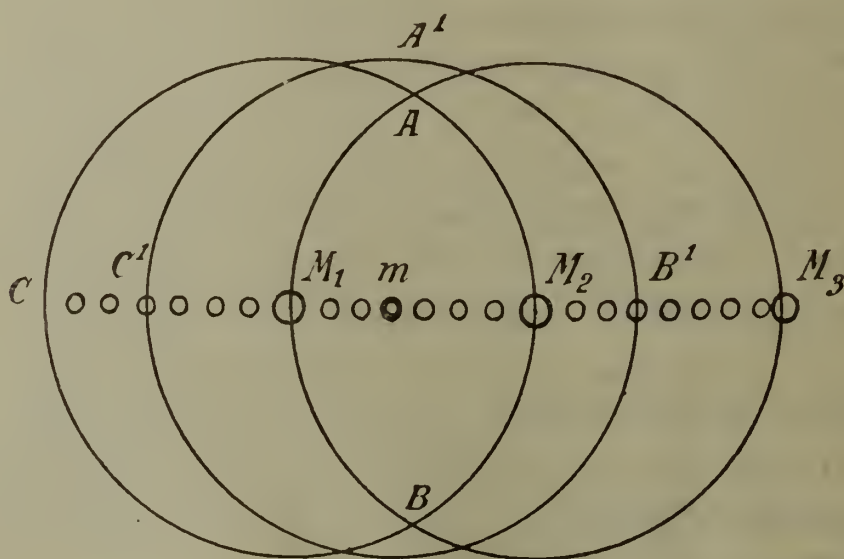


Fig. 6.

For consider any molecule M_1 of the liquid (see fig. 6); describe about M_1 the sphere of molecular activity ABC of radius E .

Now take any other molecule M_2 of the liquid which lies on this sphere of molecular activity ABC .

Then M_2 and every molecule beyond M_2 is unaffected by M_1 and vice-versa.

Consider now the molecule M_1 replaced by a foreign molecule, which is different in nature from the other surrounding molecules of the liquid.

Two cases remain to be considered.

Case I. The molecules of the liquid attract each other more strongly than they attract M_1 .

Case II. The molecules of the liquid attract M_1 , more strongly than they attract themselves.

We will first consider case I.

Consider any molecule m (fig. 5) in the interval between M_1 and M_2 . Describe about m its sphere of molecular activity $A'B'C'$.

Then m is pulled in the direction mB' by the united action of the molecules which lie in the line mB' ; similarly m is pulled in the contrary direction by the action of the molecules which lie in the line mC' . But since the foreign molecule M_1 exerts a weaker pull on m than the molecule of the liquid it has displaced, it is clear, that there will be a resultant force in the direction mB' ; and so m will tend to move away from M_1 until it passes beyond the sphere of molecular attraction AM_2B ; that is, beyond the molecule M_2 . It is clear, therefore, that every molecule of the liquid within the sphere of molecular activity of M_1 will be acted upon by a repulsive force tending to drive it away from M_1 which repulsive force will only cease when the molecule passes beyond the sphere ABC . A sort of vacuum bubble will therefore tend to form around M_1 and as the molecule M_1 moves forward, the molecules of the liquid will be drawn away from it; so that the motion of the foreign molecule will be unimpeded by the surrounding molecules of the liquid, and they will move more freely as if in a vacuum..

Cause of van't Hoff's law of osmotic pressure.

This last result puts us in a position to understand why van't Hoff's law of osmotic pressure should hold true. van't Hoff believes that a substance dissolved in a liquid exerts the same pressure on the walls of the vessel in which the solution

is contained as were the solvent imagined removed and the substance in a gaseous state were in the space occupied by the liquid.

This view has been seriously questioned by many writers of great mathematical repute. For example Prof. O. E. Meyer speaking of this conception of van't Hoff (*Kinetic Theory of Gases*. Eng. Trans. 1899. p. 367) says: "I will also not conceal that I do not think van't Hoff's views of the kinetic nature of osmotic pressure to be correct. For osmose does not arise from the kinetic pressure of the dissolved substance, but from quite different forces which cannot be neglected." These authors, however, have entirely neglected to take into account the fact that some kinds of molecules attract each other very much more intensely than they attract other kinds of molecules. For example the molecules of carbon exert an enormous attraction on each other, as is evident from the great infusibility, involatility and altogether extraordinary hardness of certain forms of carbon.

The result of this fact is, as we have just pointed out, that a foreign molecule surrounded by such molecules would travel inside of a vacuum bubble, precisely as is demanded by van't Hoff's conception. The latter may therefore be taking as corresponding to an actual physical reality.

Case II. When the molecules of the liquid attract the foreign molecules more strongly than they attract each other. In this case the molecules A of the liquid would combine with the foreign molecules B, to form a new molecule — the combination continuing until the new compound thus formed is attracted by the molecules of the liquid less strongly than they attract each other; the case then resolves itself into case I previously considered, but with the difference that the new unit is not the original molecule B, but the compound formed with B and the molecules of the liquid. Traces of such compounds are very often met with in solution and the above is the explanation of their occurrence.

The facts quoted in the last chapter make it evident that in general when a molecule adds on atoms to itself, the intensity of the attraction it exerts on other molecules in general decreases. For example high-grade valency compounds are al-

most always more volatile than low-grade compounds of the same molecular weight. Saturated organic compounds are more volatile than unsaturated compounds of the same molecular weight. Unstable compounds are usually more volatile and fusible than stable compounds of the same molecular weight, and the addition of atoms to a molecule decreases its stability. Many illustrations of this phenomenon have been given in the preceding chapter (see pp. 120—123) and there can be little doubt that it is a general law that the intensity of the attraction decreases as the number of atoms added on increases.

So that, in general, combination of the liquid and the dissolved molecules will continue until the new compound thus formed is attracted by the molecules of the liquid less strongly than they attract themselves; so that all cases of solution resolve themselves into case I.

Magnitude of the repulsive force exerted on m at any distance d from m .

The repulsive force R exerted on m (see fig. 6) at a distance d from M_1 is clearly the difference in the intensity of the force which a molecule of the liquid if at M_1 would exert on m , and the force which the foreign molecule M_1 actually exerts (compare Archimedes principle in hydrostatics).

If at a distance d a liquid molecule exerts on m a force $F(d)$
 " " " " " " foreign " " " " " " $f(d)$.

Then the repulsive force R acting on m at a distance d is:

$$R = F(d) - f(d) \dots \dots (1)$$

If we assume (as is always done in molecular physics, principally because it is convenient) that the law with which the force decays with the distance is the same for all kinds of molecules, then equation (1) takes a simpler form, for $f(d)$ now becomes $k.F(d)$, where k is a constant less than unity and hence:

$$R = (1-k) F(d) \dots \dots (2)$$

If the foreign molecules exert forces of the same intensity as the liquid molecules that they displace, then in (1) $F(d)=(fd)$ and $R=0$; in (2) $k=1$ and again $R=0$.

This occurs when the compounds are chemically similar as we previously proved. It is owing to this fact, as we shall presently show, that chemically similar substances are miscible in all proportions.

Limit of solubility.

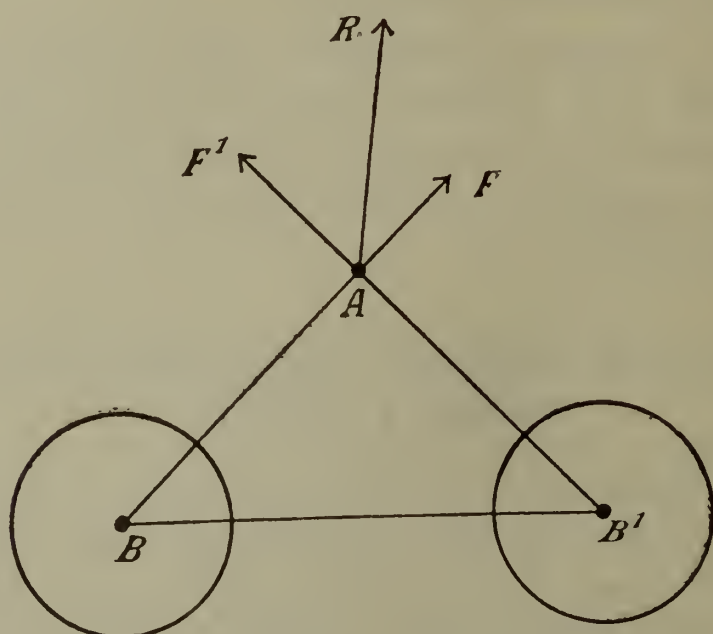


Fig. 7.

Consider the molecule B of the foreign substance travelling in the middle of a "vacuum bubble" in the interior of the liquid. (fig. 7). Suppose now a molecule A of the liquid to move towards B. Then as it approaches the surface of the bubble it will begin to be acted upon by a force tending to pull it backwards into the liquid.

Consider now two foreign molecules B and B' to be close together; and consider a molecule A of the liquid situated as in the figure. Then A will be attracted away from B in the direction AF, and away from B' in the direction AF'. Consequently there will be a resultant action on A, directed away from the line BB' joining the centres of the molecules B, B'. Conse-

quently the two molecules BB' will tend to draw together in the liquid, so soon as B comes within the sphere of attraction of B' . Now before the molecule A of the liquid will begin to be repelled away from the line BB' , the force exerted on A must be of an appreciable magnitude F , namely, of a magnitude great enough to curve appreciably the path of A within the time t it is under the influence of B and B' (see section "sphere of molecular activity" p. 125). Consequently so long as the molecules B, B' are at such a distance apart that the force exerted on A is smaller than F , A will not tend to move away from the line BB' , and so B and B' when at this distance will not tend to come together.

Whence we arrive at the cause of the limited solubility of one body in another: a liquid can only contain so many molecules dissolved, that the average distance between any two of these molecules is greater than the distance d at which the repulsive force R reaches a certain minimum value F , depending upon the temperature, molecular weight, and nature of the liquid.

If more than this number of molecules are dissolved in the liquid, the molecules will draw together and separate out until the average distance between the molecules remaining in the liquid is greater than this critical distance.

Why in general the solubility increases with increase of temperature, and diminishes with fall of temperature.

It has been shown (p. 125) that the molecules of the liquid can approach nearer to the dissolved molecule without being repelled, when the liquid is hot than when it is cold, this result being due to the increase of kinetic energy of the molecules of the liquid with the temperature.

So that B and B' can approach nearer together without being drawn together, when the liquid in which they are immersed is hot than when it is cold. So that in general, the solubility of the molecules of B in the liquid A must increase or decrease according as the temperature increases or decreases.

Why chemically similar substances are miscible in all proportions and chemically unlike substances usually immiscible.

The repulsive force (see p. 125) exerted on a foreign molecule is

$$R = F(d) - f(d)$$

or more probably $R = (1-k) F(d)$

If the two compounds are chemically similar, they exert forces of the same intensity; consequently $f(d) = F(d)$ or $k = 1$. (See theory of chemical similarity, chap. II).

So that $R = 0$, and the minimum repulsive force F is never attained. Consequently the two molecules B, B' do not tend to draw together and separate out. Hence in this case the molecules of B are miscible in all proportions among the molecules of A .

If, however, the two substances are not chemically similar, then in general R has always a finite magnitude and so the two liquids will separate out into two layers until the distance between the molecules of B remaining in the liquid become of more than the critical distance d apart, as previously described.

The case, in fact, is strictly analogous to what occurs in hydrostatics; for in precisely the same way that a cork tends to be expelled out of water because it exerts a different gravitational force to the water it has displaced; so also a dissimilar molecule tends to be expelled from out of the molecular interstices of a liquid, because it exerts a different attractive force on the surrounding molecules of the liquid to that which the molecule of the liquid which it has displaced exerts. Similarly just as a substance of the same density as water does not tend to be expelled out of it, because it exerts a gravitational force of the same intensity as the water it has displaced; so also a chemically similar molecule does not tend to be expelled from out the intermolecular interstices of a liquid, because it exerts a force of the same intensity as the molecule of the liquid which it has displaced.

Why molecules often dissociate when they pass into solution.

A molecule A in the interior of a liquid is surrounded equally on every side by other molecules, each of which exerts an attractive force on it. The molecule A is therefore subjected to an outward tension equally directed in all directions, the magnitude of this internal tension being called by Lord Rayleigh the "Internal Pressure" of the liquid.

If the molecule A is not of a rigid enough constitution, it would tend to expand out in every direction under the action of these attractive forces. This is the reason why so many molecular systems, when they pass into solution, decompose under this strain into their constituent atoms or ions.

In fact, it is only when the attractive forces holding the constituent parts of the molecule together are greater than the attraction exerted on them by the surrounding molecules, that they hold together undissociated in the liquid.



Chapter IV.

The normal affinity surfaces of the elements.

Practical construction of the normal affinity surfaces.

Practical difficulties cause us to deviate somewhat from the method of constructing affinity surfaces given in chapter 1.

We first plot out the Periodic System upon a flat surface, the group numbers being plotted along OX and the series numbers along OY precisely as in chapter 1, the position of every element being indicated by a point. (See fig. 1, chap. 1. p. 22).

We now take the given atomic species A whose affinity surface it is required to construct, and estimate in the way we will presently describe the attractive forces it exerts on the atoms of the various elements of the Periodic System. We will then erect a perpendicular from every point in the diagram, of a length proportional to the attractive force which A exerts on the element represented by that point. We now describe a surface through the summits of these perpendiculars. Then the shape of the surface represents at a glance the relative magnitude of the affinities exerted by the element A on the different elements of the Periodic System.

The surface thus obtained is the required affinity surface of A. A surface constructed in this way will, in practice, be found to resolve itself into two distinct surfaces, one corresponding to the elements of the odd series of the Periodic System, and the other to the elements of the even series.

For convenience we will resolve the Periodic System into the two following primary systems A and B and construct a characteristic surface for each system:

Primary system A:

Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
Cu	Zn	Ga	Ge	As	Se	Br	Kr
Ag	Cd	In	Sn	Sb	Te	I	Xe
Au	Hg	Tl	Pb	Bi	—	—	—

Primary system B:

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Rb	Sr	Y	Zr	Nb	Mo	—	Ru	Rh	Pd
Cs	Ba	La	Ce	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—
—	—	—	—	Ta	W	—	Os	Ir	Pt
—	Ra?	—	Th	—	Ur	—	—	—	—

Unfortunately, many of the elements of the primary system B are rare and imperfectly known; others wholly wanting.

We are therefore forced, for the present, to confine ourselves solely to the consideration of the affinity surface relating to the primary system A, which indeed is quite sufficient for our purpose.

To determine the relative magnitudes of the affinities of any given element, we study the available data as regards the stability of its compounds. For in general the intensity of the attraction which the atoms of such an element as, say, oxygen exerts on an atomic species A, may be measured by the ease or difficulty with which oxygen can be removed from its combinations with that atomic species.

For example, PbO is easier to reduce to Pb than In_2O_3 to In; and harder to reduce to Pb than HgO is to reduce to Hg. We hence conclude that oxygen attracts Pb with a smaller intensity of force than it attracts In; and with a greater intensity of force than it attracts Hg.

Hence in constructing the affinity surface for oxygen, the perpendicular drawn through In should be longer than the per-

pendicular drawn through Pb; and this latter perpendicular should be longer than the perpendicular drawn through Hg.

By proceeding in this way for the oxides of all the elements, it is a matter of comparative ease to arrive at a general notion of the form of the affinity surface for oxygen.

But the actual magnitude of these affinities is a question of much greater difficulty.

Thermal data give us valuable indications in this respect; but even here it is not a reliable guide, since the thermal values given are merely difference effects, and not the true heats of formation of compounds.

In fact, in the present state of chemical science it is impossible to represent quantitatively the form of the affinity surface of the various elements, though the general qualitative shape is comparatively easy to determine by merely studying minutely the chemical reactions and stability of the compounds of the elements.

The affinity surfaces we here give are to be regarded as not in any sense accurately giving the absolute magnitudes of the affinities of an element, but merely a general notion of the relative magnitudes.

The results as they are, are sufficiently remarkable.

We must now say a few words as regards the scale on which the attractions the elements exert on each other are measured.

Where the heat of formation is large we take this as measuring the attractive force; and the ordinates are erected of a length proportional to these magnitudes.

When the heat of formation is great, every 4000 calories evolved in the formation of the compound counts as a unit length of the perpendicular on the scale of the diagram; to give an example, we have $(\text{Li}, \text{Br}) = 80,000$; whence to determine the height of the perpendicular proportional to the attraction which Li exerts on Br, we divide the 80,000 by 4000 and get

$$\frac{80,000}{4000} = 20$$

So that length of the perpendicular representing the force with which Li attracts Br (or Br attracts Li), is taken as 20. In

cases where the heats of formation are very small or even negative, this method of measurement does not hold, for reasons stated in chapter 2. p. 47. For example when a compound (such as HI or SeH_2) has a negative or zero heat of formation, we do not assume that the constituent atoms in the molecule exert a negative (i. e. repulsive) or zero attractive force on each other — were this the case the atoms could not aggregate together at all — but we assume that they have actually a small positive affinity for each other.

The numbers attributed to the attractions which a given element exerts on the other elements is always stated in the description of the affinity surface of this element; these numbers being derived where possible by means of thermal data in the manner above described; and where this fails or is insufficient, by a comparative study of the compound, which enables us to decide with a considerable degree of precision the attractive force which the elements exert on each other.

We give a drawing and description of the normal affinity surface of the following elements: H, Li, Na, K, Cu, Ag, Au, Mg, Zn, Cd, Hg, B, Al, Tl, C, Si, Sn, Pb, N, P, As, Sb, Bi, O, S, Se, Te, F, Cl, Br, I.

And we give in 14 large plates a survey of the stability of the compounds of H, Li, Na, Mg, B, Al, C, Si, N, P, O, S, F, Cl; from which data the affinity surfaces were constructed. The space at my disposal has prevented me from reproducing here these plates for the other elements, although I have constructed them for all the elements above mentioned, as indeed is necessary before we can construct the affinity surfaces of those elements. The data in the tables given are complete to the end of 1903.

Description of the affinity surfaces (normal) for the primary system A of some elements.

We now proceed to describe the normal affinity surfaces of the 31 elements mentioned on p. 137. The best way to do this is to give the cross sections and the longitudinal sections of the surface corresponding to every series of elements plotted out in the drawing of the affinity surfaces. The surfaces are exhibited on the large plate at the end of the book.

The numbers given under each cross section are the heights of the perpendiculars erected in the figures of the surfaces as proportional to the attractional force which the element to which the number is attached exerts on the element whose affinity surface is being described.

Affinity surface for Hydrogen for the primary system A Cross-sections.

1. Li, Be, B, C, N, O, F. The attraction for H falls slightly from Li to Be, reaches a minimum at B, rises somewhat at C, falls again at N, then rapidly rises until F is reached.

Li	5.4
Be	3.0
B	1.0
C	1.3
N	1.0
O	8.5
F	9.4

2. Na, Mg, Al, Si, P, S, Cl. The attraction for H is feeble at Na and remains feeble until S is reached, becoming suddenly great at Cl.

Na	1.6	Si	1.0
Mg	1.2	P	1.8
Al	1.0	S	0.6
Cl	5.5		

3. Cu, Zn, Ga, Ge, As, Se, Br. The attraction for H is very feeble at Cu, and probably still more feeble at Zn, Ga, Ge.

H and H.

Hydrogen atoms possess a considerable affinity for each other, combining together to form H_2 . Nascent hydrogen is in an unstable condition, consisting of only single atoms.

Data for determining the intensity of the force with which Hydrogen attracts the various elements of the primary system A.

Li and H $[Li, H] = 21,600$. Stable solid. Decomposed slightly at 480° . Decomposed by water with liberation of H. Heated in air or chlorine, it burns. At ordinary temps is unaffected by Cl. H attracts Li 1. more strongly than Na, 2. probably more strongly than Be.	BeH₂ . Has been obtained in small quantities by Winkler (1891) by reducing BeO with Mg in a current of H. Not very stable, but capable of existing in part at a bright red heat. Decomposed by H_2O , evolving H. Heated in O burns with an H flame. H attracts Be 1. probably less strongly than Li, 2. more strongly than B.	BH₃ . $[B^{1/3}, H] < [Si^{1/4}, H] < 8,200$ $[C^{1/4}, H] < 5,400$ Not yet obtained free from H. Passed thro' a glass tube heated to a dull red heat, is completely decomposed to B and H. Is decomposed by electric sparks to B and H; unstable body. H attracts B 1. less strongly than Be, 2. less strongly than C?	CH₄ . $[C^{1/4}, H] = 5,400$. Stable. When passed through a red hot tube it is for the most part unaffected. H attracts C 1. more strongly than B? 2. more strongly than N? 3. more strongly than Si?	NH₃ . $[N^{1/3}, H] = 4,000$. Decomposed to N and H when passed through an iron tube at 500° . Decomposed to N and H by passing over metals such as Au, Pt, Fe, &c at 700° . Burns when heated in air or O. H attracts N 1. somewhat less strongly than C, 2. much less strongly than O, 3. somewhat more strongly than P.	OH₂ . $[H, O^{1/2}] = 34,200$. Decomposed partially at a white heat (melting point of Pt into H and O). Stable body. H attracts O 1. more strongly than N, 2. less strongly than F, 3. much more strongly than S.	FH . $[H, F] = 37,600$. Gas. Stable at a very high temp ^o . F decomposes water at ordinary temps ^o , evolving O and hence attracts H more strongly than O. H attracts F 1. more strongly than O, 2. more strongly than Cl.
Na and H $[Na, H^{1/2}] = 6,500$. Can be melted without decomposition in H. Heated in vacuo a regular dissociation takes place from 330° to 430° . Unstable body, less stable than LiH, more stable than CuH. H attracts Na 1. less strongly than Li, 2. more strongly than Cu, 3. probably less strongly than Mg.	MgH₂ . Obtained in small quantities by Winkler (1890) by heating MgO with Mg in a current of H. Evolves H when treated with warm water. H attracts Mg 1. more strongly than Na.	AlH₃ . Unknown.	SiH₄ . $[Si^{1/4}, H] = 8,200$. Is decomposed completely to Si and H by heating above 400° . Takes fire in the air when slightly heated. Is much less stable than CH ₄ . H attracts Si 1. less strongly than C, although SiH ₄ has a greater H-F than CH ₄ , 2. more strongly than Ge.	PH₃ . $[P^{1/3}, H] = 3,860$. Is very unstable. Decomposed by light. Easily decomposed by heat by passing through a red hot tube. Burns in air at 150° . Decomposed by electric sparks. H attracts P 1. somewhat less strongly than N, 2. more strongly than As, 3. less strongly than Si, 4. more strongly than S.	SH₂ . $[S^{1/2}, H] = 2,300$. Is easily decomposed. When heated to c. 400° is decomposed to H and S, also decomposed by electric sparks. H attracts S 1. much less strongly than O, 2. more strongly than Se, 3. less strongly than P, 4. much less strongly than Cl.	ClH . $[H, Cl] = 22,000$. Gas. Decomposed by heat at about 1500° into H and Cl. Not combustible. H attracts Cl 1. less strongly than F, 2. more strongly than Br, 3. much more strongly than S.
Cu and H . Brown powder, very unstable body. Decomposes at 60° to Cu and H. It takes fire in Cl. Cu has but a feeble affinity for H. H attracts Cu 1. less strongly than Na, 2. more strongly than Ag.	ZnH₂ . Unknown.	GaH₃ . Unknown.	GeH₄ . Very unstable, gaseous, body. Decomposed by heat like AsH ₃ and SbH ₃ giving a metallic mirror. Is less stable than SiH ₄ or AsH ₃ , prepared GeCl ₄ + Na amal. H attracts Ge 1. less strongly than As, 2. less strongly than Si, 3. more strongly than Sn.	AsH₃ . $[As^{1/3}, H] = -12,200$. Very unstable. Easily decomposed into As and H by heat even in the presence of much H. Heated in air burns to $As_2O_3 + H_2O$. H attracts As 1. less strongly than P, 2. more strongly than Sb, 3. less strongly than Se.	SeH₂ . $[Se^{1/2}, H] = -9,400$. Easily decomposed by heat to Se and H. Begins to decompose at 150° . Is considerably less stable than SH ₂ . H attracts Se 1. less strongly than S, 2. more strongly than Te, 3. more strongly than As, 4. much less strongly than Br.	BrH . $[H, Br] = 8,400$. Less stable than HCl. Is stable at 700° . Not combustible. H attracts Br 1. less strongly than Cl, 2. more strongly than I, 3. more strongly than Se.
Ag and H . Said to have been obtained as a black precipitate, very unstable. Decomposed by H_2O or heat. H attracts Ag 1. less strongly than Cu, 2. more strongly than Au.	CdH₂ . Unknown.	InH₃ . Unknown.	SnH₄ . Unknown. Attempts to prepare it in the same way as GeH ₄ were unsuccessful. It appears to be too unstable to exist at ordinary temps ^o . H attracts Sn 1. less strongly than Ge, 2. less strongly than Sb, 3. probably more strongly than Pb.	SbH₃ . $[Sb^{1/3}, H] = -28,1$. Very unstable. Easily decomposed by heat into Sb and H: or by long contact with H_2O . Heated in air explodes to $Sb_2O_3 + H_2O$. Less stable than AsH ₃ . H attracts Sb 1. less strongly than As, 2. more strongly than Bi, 3. less strongly than Te, 4. more strongly than Sn.	TeH₂ . $[Te^{1/2}, H] = -17,000$. Very unstable. It soon decomposes over dry Hg even in the dark. In the presence of moist air the decomposition is instantaneous. Is easily decomposed by heat. Te attracts H 1. less strongly than Se, 2. more strongly than Sb, 3. less strongly than I.	IH . $[H, I] = -6,000$. Decomposed by heat to H and I, slowly at 180° , quickly at 440° . Heated with O, there is formed H_2O and I. Much less stable than HBr. H attracts I 1. less strongly than Br, 2. more strongly than Te.
Au and H . No hydride of Au has been isolated and is probably too unstable to exist at ordinary temps ^o . Au attracts H 1. less strongly than Ag.	HgH₂ . Unknown.	TlH₃ . Tl cannot be made to combine with H (Crookes).	PbH₄ . Unknown and probably too unstable to exist.	BiH₃ . Unknown. Probably too unstable to exist at ordinary temps ^o .		

At As the attraction for H is very small, but rises steadily from thence to Br.

Cu 0.7	Ge 0.3
Zn 0.4	As 0.3
Ga 0.3	Se 0.5
Br 2.1	

4. Ag, Cd, In, Sn, Sb, Te, I. The attraction for H is very feeble for all these elements.

Ag 0.5	Sn 0.2
Cd 0.2	Sb 0.2
In 0.2	Te 0.3
I 0.5	

Longitudinal sections.

1. Li, Na, Cu, Ag, Au. The affinity is considerable for Li and decreases steadily as we pass from Li to Au.

Li 5.0	Ag 0.5
Na 1.6	Au 0.1
Cu 0.7	

2. C, Si, Ge, Sn, Pb. The affinity is feeble for all these elements. It is greatest for C and steadily decreases as we pass from C to Pb.

C 1.3	Sn 0.2
Si 1.0	Pb 0.1
Ge 0.3	

3. N, P, As, Sb, Bi. The affinity is feeble and decreases steadily as we pass from N to Bi.

N 1.0	Sb 0.2
P 0.9	Bi 0.1
As 0.3	

4. O, S, Se, Te. The affinity is very great at O and falls rapidly as we pass from O to Te, being quite small at the latter point.

O 8.0; S 0.6; Se 0.5; Te 0.3.

5. F, Cl, Br, I. The affinity is great for F and decreases rapidly as we pass from F to I.

F 9.0; Cl 5.0; Br 2.1; I 0.5.

Lithium.

1. Li, Be, B, C, N, O, F. The attraction for Li is very small at Li, and rises steadily until F is reached, where the attraction is very great.

Li 0.2; Be 0.5; B 1.0; C 1.4; N 4.1; O 17.5; F 25.?

2. Na, Mg, Al, Si, P, S, Cl. The attraction for Li is very small for Na and rises steadily, becoming very great at Cl.

Na 0.2; Mg 0.3; Al 0.4; Si 1.3; P 3.5; S 15.0; Cl 23.5.

3. Cu, Zn, Ga, Ge, As, Se, Br. The attraction rises from Cu to Br, being great at the latter and small at the former point. Cu 0.2; Zn 0.2; Ga 0.5; Ge 1.0; As 3.0; Se 11.3; Br 200.

4. Ag, Cd, In, Sn, Sb, Te, Br. Similar to (3) only the attraction for Ag is greater, and the attraction for Br is smaller than the attractions for the corresponding elements in (3).

Ag 0.5; Cd 0.2; In 0.5; Sn 0.6; Sb 2.5; Te 9; Br 16.

5. Au, Hg, Tl, Pb, Bi. The attraction for all these elements is but feeble. Au 0.2; Hg 3; Tl 2.5; Pb 2.3; Bi 2.2.

Longitudinal sections.

1. H, Li, Na, Cu, Ag, Au. The attraction for Li is considerable at H, seems to be very small at Li, and then probably rises somewhat until Au is reached (because Hg which is next to Au has a great affinity for Li).

H 5.4; Li 0.2; Na 0.2; Cu 0.2; Ag 0.5; Au 0.5.

2. C, Si, Ge, Sn, Pb. The attraction for Li is feeble for all these elements.

C 1.4; Si 1.3; Ge 1.0; Sn 1.0; Pb 2.3.

3. N, P, As, Sb, Bi. All possess a fair attraction for Li, the attraction appearing to diminish somewhat as we go from N to Bi.

N 4.1; P 3.5; As 3.0; Sb 2.5; Bi 2.2.

HLi. [Li, H] = 21,600.

White stable solid. Is only slightly decomposed at 680°. At ordinary temps⁰ dry Cl has no action on it. Decomposed by H₂O with liberation of H. Heated in air burns, yielding oxide and H₂O. Li has a considerable affinity for H.

Data for determining the force with which the various elements of the primary system A attract Lithium.

Li and Li. Li atoms seem to have no power of combining together. Ramsay found that the molecule of Li in Hg was mostly atomic.	Be and Li. No compound known. Probably but a feeble affinity.	BLi₃. No boride been obtained (1903), but is probably capable of existing since silicides are known. The compound is probably (from analogy with the silicide) somewhat less stable than CLi.	CLi. [Li, C] = 5,650. White crystalline body. Can be prepared in electric furnace by heating Li ₂ CO ₃ + 4C, to a not too high temp ⁰ ; at high temps ⁰ in the electric furnace it is decomposed, and in a vacuum at a red heat it begins to dissociate. Decomposed by cold H ₂ O with production of C ₂ H ₂ . Li seems to attract C more strongly than it attract either B or Si, and less strongly than N.	NLi₃. [Li, N ^{1/3}] = 16,500. Li combines with N with incandescence, when heated with it to a dull red heat. Easily decomposed on heating in H to Li + NH ₃ . Decomposed by H ₂ O to form NH ₃ . Li attracts N 1. less strongly than O, 2. more strongly than C, 3. more strongly than P?	OLi₂. [Li, O ^{1/2}] = 70,600. Stable compound. Li burns in O with incandescence. Li attracts O 1. less strongly than F, 2. more strongly than N, 3. more strongly than S does.	FLi. LiF is decomposed with difficulty by aqueous HCl altho' at a red heat it is completely decomposed by HCl (which seems to indicate LiF is very slightly less stable, or of about the same degree of stability, as LiCl) or partially by steam. Thermal data is wanting, but it seems from the data probably that Li attracts F 1. more strongly than O, 2. about the same degree of strength as Cl (perhaps somewhat, but not much, more strongly).
Na and Li. Li appears to dissolve in Na, but no compound seems to have been isolated. Na, in fact, has little or no affinity for Li.	Mg and Li. No compound known. Probably very feeble affinity.	ALi₃. No compound known. Affinity probably feeble.	Si and Li. Li and Si combine directly when heated to dull redness in a vacuum. Decomposed in a vacuum, when heated above 600° into Li and Si, but is stable at 400—500°. Decomposed violently by H ₂ O. Inflames in Cl, HCl, H ₂ SO ₄ , HNO ₃ ; burns when heated in air. Heated in H to 600° yield Li ₂ H + Si; so that Li ₂ H is probably more stable than SiLi ₃ .	P and Li. According to Troost, Li and P combine, when heated together, to form a brown substance which is decomposed by H ₂ O with the evolution of PH ₃ .	SLi₂. ¹ / ₂ [Li ² , S, Aq] = 58,000. Li and S combine when heated together. Li ₂ S is obtained by reducing Li ₂ SO ₄ by an equivalent quantity of C at a full red heat. Easily soluble in H ₂ O and alcohol. Li attracts S 1. less strongly than O, 2. more strongly than P, 3. less strongly than Cl.	CLi. [Li, Cl] = 94,000. Stable body. melts at a dark red heat to a clear liquid which gives off some Cl and becomes alkaline, when heated for a long time in the air. Some change occurs when LiCl is evaporated. Completely decomposed by heating in steam, with evolution of HCl. Li attracts Cl with 1. probably about same strength as F, 2. more strongly than S, 3. more strongly than Br.
Cu and Li. No compound been isolated. Affinity feeble.	Zn and Li. No compound known. Probably very feeble affinity.	Gal₃. No compound known.	Ge and Li. No compound seems to be known.	AsLi₃. Can be prepared by heating together Li + As; or by heating Li arsenate + C in electric furnace for 2½ mins. with a current of 950 amperes and 50 volts. H ₂ O decomposes it, giving AsH ₃ . At a low red heat it burns in O. F, Cl, Br act on it in the cold with incandescence. Li probably attracts As 1. less strongly than P, 2. more strongly than Sb, 3. less strongly than Li.	SeLi₂. [Li, Se ^{1/2}] = 45,300. Li seems to possess a considerably affinity for Se. Li attracts Se 1. less strongly than S, 2. more strongly than As, 3. more strongly than Te? 4. less strongly than Br.	BrLi. [Li, Br] = 80,000. Stable body. Li attracts Br 1. less strongly than Cl, 2. more strongly than I, 3. more strongly than Se.
Ag and Li. According to Watt's Dictionary, when Li is heated together with Ag, it acts on it — probably dissolving it. However no definite compound seems to have been isolated. Affinity feeble.	Cd and Li. No compound known; probably but a feeble affinity.	InLi₃. No compound known.	SnLi₄. Lebeau (1900) states that by heating together Sn + Li a compound SnLi ₄ is formed.	SbLi₃. Sb and Li combine together with the evolution of great heat. The reaction proceeds violently. Also prepared by electrolysis LiCl will an electrode of Sb. Is easily decomposed by H ₂ O with evolution of H.	TeLi₂. No telluride of Li has been prepared; but one is almost certainly capable of existing.	Iil. [Li, I] = 64,000. Soluble in water. Seems stable. Li attracts I 1. less strongly than Br, 2. more strongly than Te.
Au and Li. According to Watt's Dictionary, when Li is heated with Au it acts on it — probably dissolving it. However no compound seems to have been isolated.	Hg and Li. Li combines with Hg with violence (like Na and K) to form an amalgam. A definite compound LiHg ₅ seems to exist. Li however does not seem to have so great an affinity for H as has Na and K, the affinity running Li < Na < K.	Tl and Li. No compound known.	Pb and Li. No compounds seems to be known.	BiLi₃. According to Lebeau, Li and Bi combine together directly with the evolution of heat.		

H₂B.

Not obtained free from H. Passed through a glass tube heated to a dull red heat is decomposed to B and H. Is decomposed by electric sparks. Unstable body.

Data for determining the force with which Boron attracts the various elements of the primary system A.

Li₂B. No boride of Li has been obtained (1903) but is probably capable of existing.	Be and B. A compound Be ₃ B ₂ C ₄ is obtained by heating BeO + B in a C crucible in the electric furnace. Hard crystals; sol. in acids; unchanged in air; superficially oxidised when heated to redness. Burns in Cl at 450°. Be possesses a perceptible affinity for B.	B and B. B atoms undoubtedly attract each other very strongly and like Si and C atoms, combine readily together. The fact that B is a very infusible and involatile element, although possessing an at-wgt. of 11 shows that this is the case. Also the existence of complex borates, of such compounds as AlB ₁₂ , Al ₂ C ₂ B ₁₂ , all indicate that B atoms have the power to combine together strongly developed.	CB and CB₂. Two compounds known. BC is produced by heating B ₂ O ₃ + C in electric furnace. Black powder. Fusible at very high temps°. Insoluble in all usual solvents, but is decomposed by fusion with alkalis. B ₂ C is formed by B + C + Fe in electric furnace black crystals. Hard enough to polish diamonds. Attacked by Cl below 1000°; not affected by O at 800°, but at 1000° it burns slowly, boiling acids are without action. B has a great affinity for C.	NB. Very stable body indeed. Formed by heating B in N. Very stable at a high temp° and very slightly acted on by most reagents — eg. by heating in air, O, I, H, HCl &c. At very high temps° it reacts with Cl to form BCl ₃ ; heated to reduces in steam forms H ₂ B ₂ O ₃ + HCl. B seems to attract N 1. probably more strongly than C, 2. probably more strongly than O does (for BN is unaffected when heated in O), 3. more strongly than P.	O₃B₂. [O ^{1/2} , B ^{1/3}] = 52.8 B burns when heated in O. B ₂ O ₃ is a very stable body. It cannot be reduced by C or H. Heated in air BN + B ₂ O ₃ are simultaneously produced. B seems to attract O 1. probably a very little less strongly than N, 2. somewhat more strongly than F? 3. much more strongly than S.	F₂B. Formed by heating B in F. Colourless gas. Acts on organic matter like conc. H ₂ SO ₄ . Incombustible. Not decomposed by electric sparks. Does not act on glass. Is very stable. Is not decomposed by Fe at a red heat. Alkali and alkaline earth metals act on it at a red heat. Forms Boro-fluorides and B. With water forms HF.BF ₃ ; or HBO ₂ .3HF. B attracts F 1. probably somewhat less strongly than O, 2. more strongly than Cl.
Na and B. No boride of Na is known.	Mg₂B₃. Winckler (1890) showed, that when Mg + B ₂ O ₃ is ignited, a mixture of Mg borate and boride is obtained. The boride Mg ₂ B ₃ was oxidisable, is attacked with difficulty by either water or alkalis.	AlB and AlB₂. Two definite compounds may be obtained by heating to redness B and Al and treating residue with HCl. AlB, thin plates, unchanged by heating in air. Dissolved by HCl and by NaOH. AlB ₂ , black crystals; very hard, unacted on by HCl, or KOH Aq. Oxidised by molten KHSO ₄ ; but not by KNO ₃ . B seems to have a very perceptible affinity for Al.	Si and B. By heating B and Si together in the electric furnace get a mixture of two different borides SiB ₃ and SiB ₆ . Both seem to be about equally stable. Decomposed by F and at higher temps° by Cl and Br. But not by I or N. Superficially oxidised by heating in air or O. Not affected by haloic acids. Slowly decomposed by conc. H ₂ SO ₄ . Rapidly decomposed by fused K ₂ CO ₃ . B has a powerful affinity for Si.	PB and P₂B₃. Besson, by heating BBr ₃ . PH ₃ to 300°, got a boride insol. in H ₂ O, reacts with boiling alkalis to give PH ₃ . Gives off P when heated to redness in N or H, according to Moissan. PB at high temps° in a vacuum loses P and goes into P ₂ B ₃ (at 1000° C in H). Not decomposed by boiling H ₂ O, but H ₂ O vapour decomposes it. At 200° in O burns. Thrown into fused alkali nitrates there is incandescence. Also Cl decomposes it with incand. B ₂ P ₃ is more stable than PB. Does not inflame in Cl or HNO ₃ . Does not burn in Cl below a red heat. B attracts P 1. less strongly than Si? 2. more strongly than S? 3. much less strongly than N, 4. more strongly than As.	S₂B₂. [S ^{1/2} , B ^{1/3}] = 13.87. White solid. Easily volatile. Unstable. Decomposed to H ₂ Se + H ₂ BO ₃ by moist air or H ₂ O — with violence in last case. Burns in Cl at ordinary temps°, in O at a red heat. S ₂ B ₂ dissociates at 390° in a vacuum into S ₂ B ₂ + S; less stable than S ₂ B ₂ . S attracts B 1. less strongly than P does, 2. less strongly than Cl does 3. less strongly than O, 4. more strongly than Se.	Cl₂B. [Cl, B ^{1/3}] = 36.6. Liquid. Fumes in air with decomposition. Is decomposed by H ₂ O to H ₂ BO ₃ . Is not decomposed by heating with Zn dust to 200°; or with Na below 150°. At 150° B separates. B attracts Cl 1. less strongly than F, 2. more strongly than Br, 3. more strongly than S.
B₂B₃? Marsch states that when Cu + amorphous B are heated together for some hours above the melting point of B, a yellow hard boride Cu ₂ B ₃ is formed. Tucker more recently 1901 showed that by heating B and Cu together in the electric furnace no boride could be obtained, and that Cu and B have very little affinity for each other.	Zn and B. No boride known.	Ga and B. No boride known.	Ge and B. No boride known.	AsB. No boride of As has been isolated. Besson showed that no boride is formed by decomposing BBr ₃ .AsH ₃ . And therefore As has a considerably less affinity for B than has P.	Se₂B₂ (?) and Se₃B₂. Two selenides seem to have been obtained, by passing H ₂ Se over B maintained at a bright red heat, viz B ₂ Se ₃ + B ₂ Se ₅ . B ₂ Se ₃ is violently decomposed by H ₂ O without separation of Se. The other (probably B ₂ Se ₅) is less volatile and is decomposed violently by H ₂ O with separation of Se. B attracts Se 1. less strongly than S, 2. probably more strongly than Te, 3. less strongly than Br.	Br₃B. Formed by action of Br on B ₂ O ₃ + C at a red heat, or by heating B in Br vapour, Colourless fuming liquid. Reacts with H ₂ O to form HBr.Aq + H ₂ BO ₃ . Less stable than BCl ₃ . More stable than Br. B attracts Br 1. less strongly than Cl, 2. more strongly than I, 3. more strongly than Se.
Ag and B. No silver boride has been obtained.	Cd and B. No boride known.	In and B. No boride known.	Sn and B. No boride known.	Sb and B. No boride known.	Te and B. No boride of Te has been isolated, but is almost certainly capable of existing.	I₃B. [B ^{1/3} , I] nearly equal [Si ^{1/4} , I] = 14.5?? Prepared by HI + B; also H + I + BCl ₃ thro' red hot tube. Colourless crystals which become rapidly coloured on exposure to light. Decomposed by H ₂ O. Heated to redness, vapour burns in air. P decomposes it in the cold with vivid incandescence. Na has no action up to 210°, but at a red heat decomposes it with incandescence. B attracts I 1. less strongly than Br, 2. more strongly than Te?
Au and B. No Au boride has been obtained.	Hg and B. No boride known.	Tl and B. No borides known.	Pb and B. No boride known.	Bi and B No boride been isolated. According to Tucker no combination takes place, when B + Bi are heated together in the electric furnace. The Bi seems to have a very small affinity for B.		

4. O, S, Se, Te. The attraction for Li appears to fall steadily as we go from O to Te.

O 17.6; S 15.0; Se 11.3; Te 9.0.

5. The attraction is great for all these elements, sinking as we pass from Cl to I.

F 23; Cl 23.5; Br 20.0; I 16.0.

Boron.

Cross-sections.

Li, Be, B, C, N, O, F. No boride of Li is known. Probably from analogy it is capable of existing, but is not possessed of any very great stability. No pure boride of Be has been isolated, although a double compound of Be, B and C is known which is possessed of considerable stability.

It seems that the attraction for B rises steadily as we pass from Li towards N, attaining a maximum at N, then slowly declining as we pass towards F.

Li 1.0; Be 4; B 8; C 10; N 14; O 13.2; F 12.5.

Na, Mg, Al, Si, P, S, Cl, Ar. No boride of Na is certainly known. Na has in all probability but a very feeble affinity for Boron. Winkler describes a boride of Mg. It would seem that the attraction for B is feeble for Na, rises from thence as we pass towards P, attains a maximum at P, then sinks somewhat, attaining a minimum at S, rising again for Cl, where it attains its greatest value.

Na 0.5; Mg 1.5; Al 2; Si 3; P 4; S 3.5; Cl 8.65.

Longitudinal-sections.

F, Cl, Br, I. The attraction for B is greatest for F and seems to fall steadily as we pass towards I; the affinity is great for all these elements.

F 12.25; Cl 8.65; Br 7.2; I 3.1.

O, S, Se, Te. The attraction for B is great at O, and falls as we pass from O towards Te.

O 13.2; S 3.5; Se 3.0; Te 2.5.

N, P, As, Sb, Bi. N has a very great affinity for B, and the affinity decreases rapidly as we pass from N towards Bi. Bi,

according to Tucker, has no affinity for B and does not combine with it when heated.

N 14; P 4; As 2; Sb 1; Bi 0.5.

C, Si, Ge, Sn, Pb. C seems to have a powerful affinity for B, and probably the affinity sinks steadily as we pass towards Pb.

C 10; Si 3; Ge 1.0; Sn 1.0; Pb 1.0.

B, Al, Ga, In, Tl. The affinity varies in the same way as in the preceding group.

B 8; Al 2; Ga 1; In 1; Tl 1.

Be, Mg, Zn, Cd, Hg. The affinity probably falls steadily as we pass from B to Hg, being probably very feeble for all these elements.

Be 1.6; Mg 1.5; Zn 1.0; Cd 0.8; Hg 0.5.

H, Li, Na, Cu, Ag, Au. H has but a feeble affinity for B; Cu seems to have no appreciable affinity for B, and cannot be made to combine with it when heated together in the electric furnace. No borides of the other elements of this group have been obtained; all have probably only a very feeble affinity for B.

C a r b o n .

Cross Sections.

Li, Be, B, C, N, O, F. The attraction for C is not great at Li, rises considerably from Li to Be, and still more from Be to B, attaining a maximum at C. It then sinks rapidly from C to N, attaining at N a minimum; it then rises from N to O, and falls somewhat from O to F.

Li 1.41; Be 2.5; B 9.0; C 18; N 0.5; O 6.1; F 5.0.

Na, Mg, Al, Si, P, S, Cl. The attraction for C is small at Ca: rises somewhat at Mg, then increases rapidly until Si is reached. It then falls, reaches a minimum at S, and rises again at Cl.

Na 0.5; Mg 1.5; Al 2.0; Si 13; P 2; S 0.5; Cl 3.4.

L o n g i t u d i n a l S e c t i o n s .

H, Li, Na, Cu, Ag, Au. The attraction is considerable for H, rises somewhat from H to Li, then falls steadily, becoming very small for Au.

H 1.35; Li 1.4; Na 0.5; Cu 0.4; Ag 0.3; Au 0.2.

H and C. $[H, C] = 5,400$.

CH_4 . Stable. When passed thro' a red hot tube it is for the most part unaffected. Electric sparks partially decompose it to C, H, and C_2H_2 . When passed over red hot Pt is decomposed to C and H. C attracts H less strongly than Li.

Li_2C_2 . $[Li, C] = 5,650$.

Crystalline body. Prepared in electric furnace by heating $Li_2CO_3 + 4C$ to a not too high temp°. At above a red heat it begins to dissociate. If the electric furnace is too hot it is completely decomposed. Decomposed by cold water with production of C_2H_2 . More stable under action of heat than NaC, or MgC, and less stable than BeC . Li attracts C

1. somewhat more strongly than H,
2. more strongly than Na,
3. less strongly than Be.

BeC_2 .

Prepared by electric furnace by heating $BeO + C$ crystals. Very hard. Decomposed by H_2O evolving CH_4 , but the action is only slow. O produces superficial oxidation at a dull red heat. Not oxidised by KNO_3 or $KClO_3$, but K_2MnO_3 and PbO_2 oxidise it readily. BeC_2 is thus a stable body.

- Be attracts C
1. more strongly than Li,
 2. more strongly than Mg,
 3. less strongly than B.

B and C.

Two compounds $BC + B_2C$ exist. BC produced by heating $B_2O_3 + C$ in electric furnace. Black powder. Fusible at a very high temp°. Burns with difficulty in O. Is insol. in all the usual solvents, but is decomposed by fusion with alkalis.

B_2C . Formed by $B + C + Fe$ in electric furnace. Black crystals. So hard, that it polishes diamonds. Attacked by Cl below 1000° . Not affected by boiling acids, nor in O at 800° , but at 1000° . The carbide burns slowly and with greater difficulty than the diamond.

- C seems to attract B
1. more strongly than Be,
 2. less strongly than C,
 3. more strongly than Al.

C and C.

Carbon atoms possess a very intense attractive power for each other. The great involatility and infusibility of all forms of carbon, and the extraordinary hardness of the diamond all arise from the intense force, with which C atoms cohere together.

Carbon is in fact the most involatile and infusible as well as the hardest substance known.

The extraordinary capacity C atoms have of combining together in organic chemistry, as well as its chemical inertness at ordinary temps° are also consequences of the same fact.

- C attracts C
1. much more strongly than B,
 2. very much more strongly than N,
 3. more strongly than Si?

N_2C_2 . $[C^{1/4}, N^{1/4}] = -8,200$.

C combines directly with N in electric arc to form C_3N_2 . Gas. Burns with a purple flame when heated in air. Heated to 500° it polymerises. At about 1200° N is liberated. Heated in presence of Fe or Pt, C and N is formed. Decomposed to C and N by electric sparks.

- C attracts N
1. less strongly than C (much less),
 2. much less strongly than O,
 3. probably less strongly than P?

O and C. $1/2[C, O] = 24,240$.

$1/2[C, O] = 14,500$. C burns in O when heated to form CO_2 . CO_2 is reduced to C by heating strongly with Na, Mg or K. Reduced to CO by heating with H, C or Fe. Partially decomposed to $CO + O$ at 1300° C. CO itself is partially decomposed to C + CO_2 at the same temp°.

- C attracts O
1. much more strongly than N,
 2. more strongly than S,
 3. more strongly than F.

F and C.

F and C combine with great energy at ordinary temps° evolving heat and light. Below a red heat CF_3 is formed. Above a red heat C_2F_4 is formed. Both fluorides when heated decompose and polymerise. CF_4 is decomposed by glass or by alcoholic KOH. C_2F_4 is more stable. Not decomposed by electric sparks.

- C attracts F
1. less strongly than O,
 2. more strongly than Cl.

Na_2C_2 . $[Na, C] = -1,480$.

White solid. Not sensitive to shock or friction, very chemically active, more so than CaC_2 . Cannot be obtained in the electric furnace because it decomposes to Na and C at temps° considerably lower than that of the arc. Dissociates to C and Na when heated to redness in a vacuum, violently decomposed by H_2O evolving C_2H_2 . NaC is less stable than either LiC or MgC.

- Na attracts C
1. less than Li,
 2. less than Mg,
 3. but more strongly than Cu.

MgC_2 .

Is too unstable to be produced in electric furnace since it is decomposed in the arc. from a current of 600 amperes and 600 volts. Can be produced mixed with C by heating, Mg powder in a stream of C_2H_2 . Is completely decomposed by H_2O with evolution of gas. MgC_2 is less stable than BeC_2 , and more than NaC.

- Be attracts Mg
1. less strongly than Be,
 2. more strongly than Na,
 3. less strongly than Al,
 4. probably more strongly than Zn does?

Al_4C_3 .

Prepared by heating Al and C, or C and Clay in electric furnace, 5-6 mins in a current of 300 amperes and 60 volts. It is decomposed at higher temps° in the electric arc. Cl attacks carbide at a dull red heat with incandescence.

O only attacks it superficially at a dull red heat. S attacks it readily with great development of heat. Slightly heated with K_2MnO_4 is oxidised with vivid incandescence. Decomposed slowly by H_2O forming CH_4 . Acids usually attack it very slowly.

- C attracts Al
1. more strongly than Mg,
 2. less strongly than Si,
 3. less strongly than B.

C and Si.

C and Si readily unite in a fused medium at 1300° to 1400° C. Also formed by $C + SiO_2$ in electric furnace. Is a body of altogether extraordinary stability. Not affected by O at temp° of Blow pipe. S vapour is without action. Cl at 600° attacks slowly, action complete at 1200° . Fused KNO_3 , $KClO_3$, boiling H_2SO_4 , HNO_3 , HCl, &c. do not attack it. Fused $PbCrO_4$ oxidises it with difficulty. It is very hard, between corundum and diamond.

- C attracts Si
1. less strongly than C?
 2. more strongly than Al,
 3. more strongly than P?

P and C.

No carbide of P has been isolated, but almost certainly one is capable of existing.

S and C.

$[C^{1/4}, S^{1/2}] = -6,500$. C and S combine directly when heated. Volatile liquid. Easily inflammable. Heated strongly gives C and S. Burns in air to SO_2 and CO_2 . Decomposed by many metals. H when passed with CS_2 over Pt gives $C + H_2S$. Chlorine decomposes it. A compound SC is also known. At 200° gives C and S.

- C attracts S
1. less strongly than O,
 2. more strongly than Se,
 3. less strongly than Cl.

Cl and C. $[C^{1/4}, Cl] = 13,500$.

Several chlorides as CCl_4 ; C_2Cl_6 ; CCl_4 are known. CCl_4 when passed thro' a hot tube gives C_2Cl_4 , C_2Cl_6 and C. Heated with SO_2 gives $COCl_2 + S_2O_5Cl_2$. With P_2O_5 gives $POCl_3 + COCl_2$. Decomposed by electric sparks. C does not combine even at very high temps°, with Cl.

- Cl attracts C
1. less strongly than F,
 2. more strongly than Br,
 3. more strongly than S.

Hg_2C_2 .

Explosive body. Cannot be prepared by heating Cu and C directly. Is prepared by passing H_2C_2 thro' Cu solutions. Decomposes when heated to 50° C to Cu and C with explosion.

- Cu attracts Cu
1. less strongly than Na,
 2. more strongly than Ag,
 3. probably less strongly than Zn?

ZnC_2 .

Not yet been prepared, but probably less stable than MgC_2 and more stable than CuC.

Ga and C.

No carbide known.

Ge and C.

No carbide known.

As_2C_2 .

No carbide known.

Se and C.

C and Se do not combine directly when heated and no definite compound has been obtained. Rathke obtained a liquid which probably contained about 2% of a selenide of C (along with CCl_4) by heating selenide of P with moist CCl_4 .

- C probably attracts Se
1. less strongly than S,
 2. more strongly than Te,
 3. less strongly than Br.

Br and C.

CBr_3 , C_2Br_4 , C_3Br_5 are known. CBr_3 boils at 189.5° C with partial decomposition. Partially decomposed with liberation of Br at 200° . Decomposed by alcohol at 100° C.

C_2Br_4 decomposes to $C_2Br_2 + Br$ at 200° C. C_3Br_5 is more stable, but is decomposed by hot Zn, Cu, Fe, CuO &c. giving metallic bromide, C, and CO_2 .

- C attracts Br
1. less strongly than Cl,
 2. more strongly than I,
 3. more strongly than Se.

Ag_2C_2 . $[Ag, C] = -43,500$.

Very unstable body and very difficult to work with. Detonates when heated in a vacuum with production of a flame and C is deposited all around. Produced by passing C_2H_2 gas thro' an ammoniacal Ag solution.

- Ag attracts C
1. less strongly than Cu,
 2. more strongly than Au,
 3. probably less strongly than Cd?

CdC_2 .

Not yet been prepared, but probably less stable than ZnC_2 and more stable than HgC_2 .

In and C.

No carbide known.

Sn and C.

No carbide known.

Sb and C.

No carbide known.

Te_2C .

No carbide of Te has been isolated. Probably very unstable.

I and C.

When CI_4 is exposed to light in a vacuum, or heated to 120° C in a vacuum, it splits up into $C_2I_4 + I$. CI_4 is easily decomposed by heat to C and I. Warmed gently in dry O it decomposes into and Cl. Reacts violently with S, P, Cl &c. C_2I_4 melts at 184° without decomposition, and begins to decompose at 200° .

- C attracts I
1. less strongly than Br,
 2. more strongly than Te.

Au_2C_2 .

Yellow explosive precipitate produced when C_2H_2 is passed into a solution of Aurous thiosulphate. Is decomposed by HCl into C_2H_2 and AuCl. Also by boiling in H_2O it goes into Au and C. Altho' very explosive it can be decomposed without explosion by very gradual heating.

- Au attracts C
1. probably less strongly than Ag,
 2. less strongly than Hg.

HgC_2 .

Results as a heavy white powder by passing C_2H_2 thro' freshly pp'd. HgO suspended in H_2O . Insol. in H_2O . Slowly decomposed by gradual heating about 110° , into Hg and C. The compound explodes by rapid heating or a blow. Altho' it explodes when struck sharply, it can be handled with safety. It is more stable than AgC or AuC .

- C attracts Hg
1. less strongly than Cd?
 2. more strongly than Au,
 3. less strongly than Ti?

Tl and C.

No carbide known.

Pb and C.

No carbide known.

Bi and C.

No carbide known.

H₃N. [N^{1/3}, H] = 4,000.
Decomposes at 500° C into N and H. Mixed with O and heated, N₃H burns.

Data for determining the force with which the various elements of the primary system A attracts Nitrogen.

<p>Li₃N. [Li, N^{1/3}] = 16,500. Li combines with N with incandescence, when heated to a dull red heat in N gas. Easily decomposed on heating in H to Li and NH₃. Decomposed by H₂O to form NH₃. N attracts Li 1. more strongly than H, 2. more strongly than Na, 3. probably less strongly than Be?</p>	<p>Be and N. No nitride of Be has as yet been isolated, but is almost certainly capable of existing intermediate in stability between Li₃N and BN.</p>	<p>B and N. BN is a very stable body formed by heating B in N. Very stable at a high temp^o and very slightly acted on by most reagents — eg by heating in air, O, I, H, HCl, &c. At a very high temp^o reacts with Cl to form BCl₃. Heated to redness in steam get NH₃ and H₃BO₃ formed. B attracts N 1. much more strongly than Be or C, 2. more strongly than Al, 3. a little more strongly than Si.</p>	<p>C₂N₂. [N^{1/3}, O^{1/3}] = 11,250. Not very stable. Polymerises on heating to 500°C. At 1200° C N is evolved. Burns when heated in O. Strong heating with Fe decomposes it to C and N. N attracts C 1. much less strongly than B, 2. much less strongly than Si.</p>	<p>N and N. N₂ seems to be a perfectly stable form of union. N₃ alone is unknown, but is known in various compounds eg. in H.N₃. The linkage — N = N — often occurs in organic chemistry. In general, the N linkages are unstable and N has but a feeble affinity for itself.</p>	<p>O and N. [N^{1/3}, O^{1/3}] = —,670. N and O forms several oxides, N₂O, NO, NO₂, &c. all of which are characterised by their instability and the ease with which they can be decomposed into O and N. NO₂ for example is completely decomposed to NO + O at 600° C, beginning to dissociate at about 180° C. N attracts O 1. more strongly than F, 2. more strongly than S.</p>	<p>F₃N. Unknown. But would probably be even more unstable than NCl₃ since the stability of the nitrides decreases as we pass from Nl₃ to NCl₃. NF₃ cannot be prepared by methods analogous to those by which NCl₃ or Nl₃ are prepared. N attracts F 1. less strongly than O, 2. less strongly than Cl.</p>
<p>Na₃N. Has not with certainty been prepared; though probably capable of existing. NaNH₂ decomposes at 500°C to Na + H + N. KNH₂ under similar circumstances also decomposes, but is somewhat more stable. Na attracts N 1. less strongly than Li, 2. more strongly than Cu? 3. less strongly than Mg.</p>	<p>Mg₃N₂. Formed by heating Mg in N, or by heating Mg and NH₃ together when a sudden glowing is observed. Is stable in N at a very high temp^o. Heated in air is slowly oxidised to MgO, oxidation is rapid in O. With H₂O forms MgO + NH₃. Heated in HCl get MgCl₂ + NH₃Cl. N attracts Mg 1. probably less strongly than Be, 2. more strongly than Zn, 3. more strongly than Na, 4. less strongly than Al?</p>	<p>Al and N. Al combine with N when heated to a very high temp^o. AlN is formed in the electric arc. Slowly decomposed by moist air to form Al₂O₃ + NH₃. Somewhat more readily by boiling H₂O and most readily by alkalis, evolving N as NH₃. N attracts Al 1. more strongly than Mg, 2. less strongly than Si, 3. less strongly than B, 4. more strongly than Ga.</p>	<p>Si₃N₄. Formed by acting on SiCl₄ with NH₃, or by heating very strongly Si in N. Infusible white powder, which is not dissolved by any acid except HF.Aq. which produces NH₄SiF₆. Slowly decomposes in moist air, producing NH₃. Melted with KHO gives NH₃ + K silicate. N attracts Si 1. much more strongly than C, 2. more strongly than Al.</p>	<p>P₃N₅. A very stable body, only acted on by Cl at temps^o at which hard glass melts. And only at a still higher temp^o does O act on it. Only in traces decomposed by boiling water (heated in sealed tube with H₂O to 180° C goes into H₃PO₄ + NH₃). Not acted on by HNO₃. Decomposes at a bright red heat (above 1000) when heated in a vacuum, into its elements N and H. N attracts P 1. more strongly than Si, 2. more strongly than S.</p>	<p>SN. [N^{1/3}, S^{1/3}] = —10,650. Unstable body. Decomposes at 160° C with slight explosion. Explodes violently when rubbed or struck with a hammer. Slowly decomposed by H₂O, with production of NH₃ and Am sulphides. Decomposed by KON, HCl, &c. N attracts S 1. much less strongly than P 2. less strongly than O, 3. more strongly than Cl.</p>	<p>Cl₃N. [N^{1/3}, Cl] = —13,000. Extremely unstable explosive body. Decomposes when heated to 90° C. Explodes in light; by contact with organic matter &c. N attracts Cl 1. more strongly than F, 2. more strongly than S, 3. perhaps more strongly than Br?</p>
<p>Cu₃N. Unstable body. Decomposes into Cu and N at 300° C. Cu and N do not combine directly together. Cu₃N decomposes violently when heated and is only capable of existing within a narrow temp^o range. Cu has but a feeble affinity for N. N attracts Cu 1. probably less strongly than Na? 2. more strongly than Ag, 3. much less strongly than Zn.</p>	<p>Zn₃N₂. Obtained by heating Zn (NH₃)₂ to low redness. Grey solid. Unchanged by heating to redness out of contact with air. Reacts violently with H₂O to give Zn(OH)₂ + NH₃. N attracts Zn 1. less strongly than Mg, 2. more strongly than Cd, 3. much more strongly than Cu, 4. less strongly than Ga?</p>	<p>Ga and N. No nitride known.</p>	<p>Ge and N. No nitride of Ge is known.</p>	<p>As and N. No nitride known.</p>	<p>SeN. Obtained by NH₃ on SeCl₄. Yellow powder; extremely explosive and very dangerous to handle. N attracts Se 1. less strongly than Te, 2. more strongly than Br.</p>	<p>Br₃N. Said by Milton to be obtained as a red liquid, quite as explosive as NCl₃, by adding KBr to NCl₃. N attracts Br 1. with about the same force as Cl, perhaps less, 2. considerably less strongly than I.</p>
<p>Ag₃N. Is an unstable explosive body. Formed by Ag₂O + NH₃ + air. Is decomposed by H₂O into Ag₂O and NH₃ (and hence must be very unstable since Ag₂O + NH₃ are both not very stable bodies). N attracts N 1. more feebly than Cu (or H), 2. more strongly than Au, 3. probably less strongly than Cd.</p>	<p>Cd₃N₂. Unknown, but probably intermediate in stability between Zn₃N₂ and Hg₃N₂.</p>	<p>In and N. No nitride known.</p>	<p>Sn and N. No nitride of Sn is known.</p>	<p>Sb and N. No nitride of Sb known.</p>	<p>TeN. Yellow powder obtained by acting on TeCl₄ with NH₃. Detonates with great violence under percussion or when heated above 200° C. It is not, however, decomposed by H₂O. Nor dilute acids; but aqueous KOH liberates all the N in the form of NH₃.</p>	<p>Nl₃. Various compounds, eg Nl₃, NHl₂, NH₃Nl₃ &c. seem to exist. All unstable explosive substances. But are certainly much more stable than Cl₃N. NH₃Nl₃ decomposes at c. 50° C with explosion. N attracts I 1. more strongly than Br or Cl, 2. less strongly than Te.</p>
<p>Au₃N. Strong NH₃.Aq acts on Au₂O suspended in H₂O to give a black explosive powder, Au₃N, H₂O. Boiling with H₂O converts it into NAu₃. Au when heated in NH₃ does not combine, but becomes "blistered" and has its elasticity much reduced. Au₃N seems to be very unstable. N attracts Au 1. less strongly than Ag, 2. less strongly than Hg, 3. more strongly than I.</p>	<p>Hg₃N₂. Prepared by action of NH₃ on HgO. Brown, very explosive powder, but requires a higher temp^o and a stronger blow than Nl₃ to explode it. Not acted on by dil. H₂SO₄. Decomposed by strong H₂SO₄ explosively. HCl and HNO₃ also decompose it to Hg salts and Am salts. Slowly decomposed by light and water. N attracts Hg 1. less strongly than Zn (and therefore Cd?) 2. more strongly than Au.</p>	<p>Tl and N. No nitride known.</p>	<p>Pb and N. No nitride of Pb is known.</p>	<p>Bi and N. No nitride of Bi is known.</p>		

Be, Mg, Zn, Cd, Hg. The attraction for C is considerable at Be, falls somewhat from B to Mg, and becomes very small at Hg.

Be 2.5; Mg 1.5; Zn 1.0; Cd 0.8; Hg 0.5.

B, Al, Ga, In, Tl. The attraction for C is great in the case of B and sinks considerably from B to Al.

B 9; Al 2; Ga 1; In 0.8; Tl 0.6.

C, Si, Ge, Sn, Pb. C atoms attract each other very strongly, and the attraction falls as we pass from C towards Pb, being very small at the latter element.

C 18; Si 13; Ge 1; Sn 0.8; Pb 0.7.

N, P, As, Sb, Bi. The attraction for C for all these elements is probably feeble.

N 0.5; P 2.0; As 1.4; Sb 0.4; Bi 0.35.

F, Cl, Br, I. All have a considerable attraction for C, the affinity sinking as we pass from F to I.

F 5; Cl 3.1; Br 2.5; I 2.0.

Nitrogen.

Cross sections.

The affinity for nitrogen rises from Li to B, then falls attaining a minimum at C, rises again at N, and then falls, becoming very small at F.

Li 4.1; Be 5; B 8; C 0.5; N 4; O 0.2; F 0.1.

Na, Mg, Al, Si, P, S, Cl. The affinity for N is very small at Na, rises steadily attaining a maximum at P, then falls again becoming very small at Cl.

Na 1; Mg 6; Al 7; Si 9; P 11; S 0.2; Cl 0.1.

Cu, Zn, Ga, Ge, As, Se, Br. The attraction is small for Cu, rising as we pass from Cu to Zn; and remains appreciable until As is reached, then again falling, becoming very small for Se, and still smaller for Br.

Cu 0.4; Zn 3; Ga 3; Ge 3; As 3; Se 0.2; Br 0.1.

Ag, Cd, In, Sn, Sb, Te, I. The affinity is small for Ag, and for Cd. It is unknown for In, Sn, Sb, but probably rises from Ag to Sb, for Sb it is small and still smaller for I.

Ag 0.3; Cd 2.5; In 2.5; Sn 2.5; Sb 1.0; Te 0.2; I 0.15.

Au, Hg, Tl, Pb, Bi. The attraction for N is very small for all these elements.

Au 0.1; Hg 0.2; Tl 0.2; Pb 0.2; Bi 0.2.

Longitudinal sections.

H, Li, Na, Cu, Au. The attraction for N increases from H to Li and then steadily decreases until Au is reached.

H 1; Li 4.1; Na 1.0; Cu 0.4; Ag 0.3; Au 0.2.

Be, Mg, Zn, Cd, Hg. The attraction for N in the case of Be is unknown. But it is probably greater than in the case of Mg, the affinity probably reaches a maximum at Mg and then sinks, becoming very small for Hg.

Be 7; Mg 6; Zn 3; Cd 5.5; Tl 0.2.

B, Al, Ga, In, Tl. The attraction for N at B is very great, and sinks thence to Al; the affinity for the other elements is unknown, but probably sinks steadily from B to Tl.

B 8; Al 7; Ga 3; In 2.5; Tl 0.2.

C, Si, Ge, Sn, Pb. The affinity for N is feeble at C, rises greatly as we pass from C to Si. For the other elements it is unknown, but probably sinks rapidly from C to Pb.

C 0.5; Si 9.0; Ge 3.0; Sn 2.5; Pb 0.2.

N, P, As, Sb, Bi. The attraction for N rises rapidly from N to P; the attraction for the other elements is unknown, but probably is feeble, falling from As to Bi.

N 4; P 8; As 3; Sb 1; Bi 0.5

O, S, Se, Te. The affinity for N is small all through the series — sinking from O to S, remaining about the same for Se as for S, then rising somewhat for Te.

O 0.2; S 0.2; Se 0.2; Te 0.2.

F, Cl, Br, I. The attraction for N is very small for all these elements, being greatest for I, and least for F.

F 0.1; Cl 0.1; Br 0.1; I 0.15.

Oxygen.

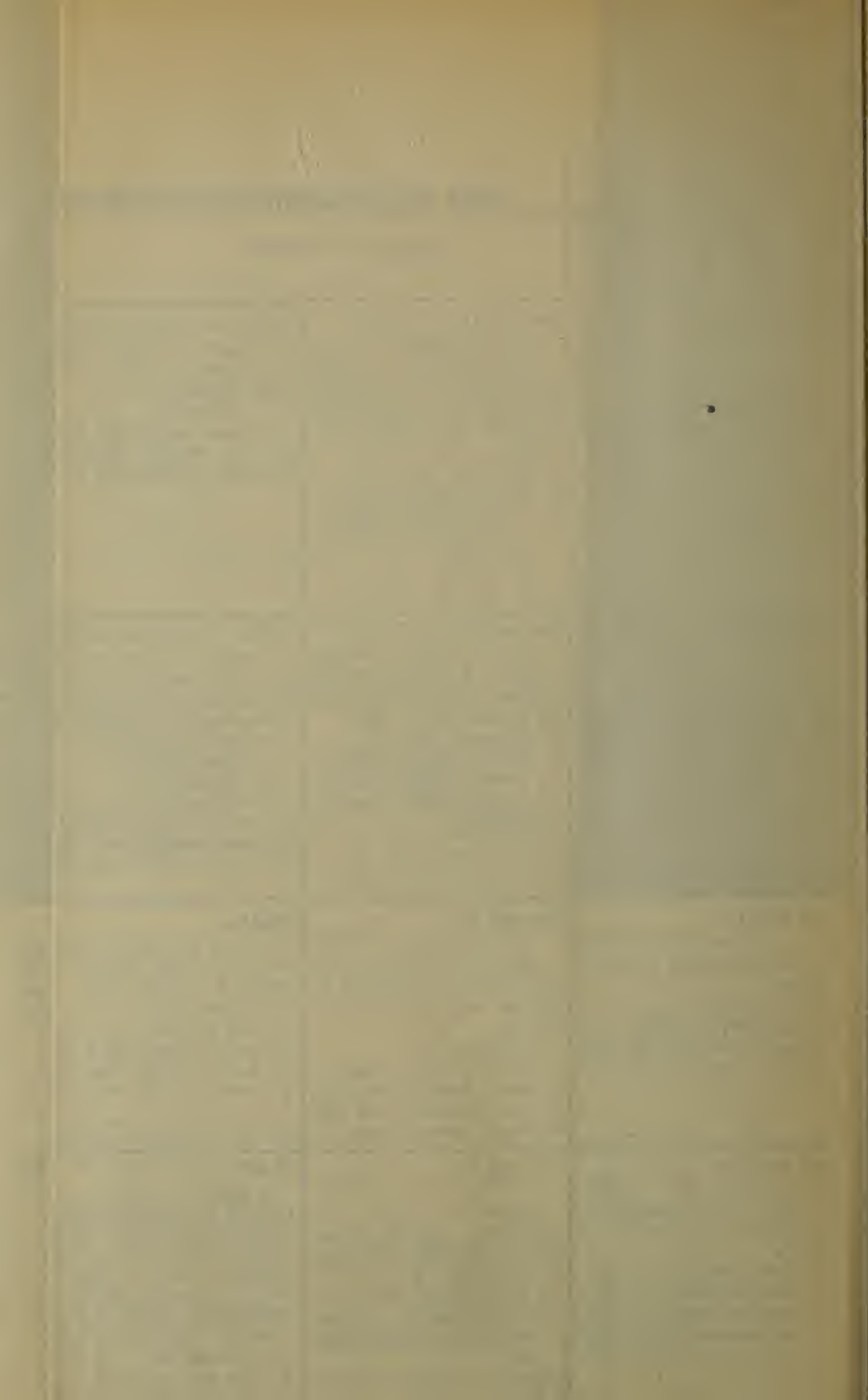
Cross Sections.

Li, Be, B, C, N, O, F. The chemical attraction for O is greatest at Li, then falls steadily, attaining a minimum at N, again

O and H.
 $[O^{1/2}, H] = 34,000.$
 H_2O is a stable body, but decomposes at the melting point of Pt (1760°).
 O attracts H less strongly than Li.

Data for determining the intensity of the force with which the various elements of the primary system A attract Oxygen.

<p>Li and O. $[Li, O^{1/2}] = 76,700.$ Li_2O is very stable. O attracts Li 1. more strongly than H 2. more strongly than Na 3. more strongly than Be</p>	<p>Be and O. BeO cannot be decomposed by heat. It seems intermediate in stability between Li_2O and B_2O_3. Probably more stable than MgO. O attracts Be 1. less strongly than Li, 2. more strongly than B, 3. a little more strongly than Mg?</p>	<p>B_2O_3. $[B^{1/2}, O^{1/2}] = 52,800.$ Cannot be reduced by C or H, and is stable at the highest temps°. O attracts B 1. less strongly than Be, 2. more strongly than C, 3. less strongly than Si.</p>	<p>C and O. $[O^{1/2}, C^{1/4}] = 24,200.$ CO_2 is reduced to C by heating strongly with Na, Mg or K. Reduced to CO by heating with H, C or Fe. Partially decomposed to CO + O at 1300° C. O attracts C 1. less strongly than B, 2. more strongly than N, 3. less strongly than Si.</p>	<p>N and O. $[O^{1/2}, N^{1/4}] = -500.$ All the oxides of N are unstable, and easily decompose into N and O. NO_2 is the most stable. It begins to decompose into NO and O at c. 180° C, and is completely decomposes at 600° C. O attracts N 1. less strongly than C, 2. less strongly than O, 3. less strongly than P.</p>	<p>O and O. O_2 is a stable body, but seems to be partially decomposed to O atoms at the melting Pt of Pt (1750°). O linkages, such as —O—O— often possess a fair degree of stability. O atoms have a very perceptible affinity for each other.</p>	<p>OF_2. No oxide of F is known. O and F are quite chemically inert towards each other. O possesses a smaller affinity for F than for Cl or O.</p>
<p>Na and O. $[Na, O^{1/2}] = 50,000.$ O attracts Na 1. less strongly than Li, 2. more strongly than Cu, 3. less strongly than Mg.</p>	<p>Mg and O. $[O^{1/2}, Mg^{1/2}] = 66,000.$ MgO is stable at the highest temps° and cannot be reduced by H or C. O attracts Mg 1. more strongly than Be, 2. more strongly than Zn, 3. slightly more strongly than Al.</p>	<p>Al_2O_3. $[O^{1/2}, Al^{1/3}] = 63,000.$ Cannot be reduced by C or H at ordinary temps°. At the temp° of the electric furnace partial reduction by C occurs. Seems stable at the highest temps°. O attracts Al 1. more strongly than B, 2. more strongly than Ga, 3. less strongly than Mg, 4. more strongly than Si.</p>	<p>Si and O. $[O^{1/2}, Si^{1/4}] = 55,000.$ Is stable at the highest temps° and cannot be reduced by H or C. Is reduced by Mg. O attracts Si 1. more strongly than C, 2. more strongly than Ge, 3. less strongly than Al, 4. more strongly than P.</p>	<p>P_2O_5. $[O^{1/2}, P^{1/5}] = 37,000.$ Is stable at a white heat. Can be reduced by heating with Fe, K, Na, probably also with C (since P is formed by reducing Phosphates with C). O attracts P 1. more strongly than N, 2. more strongly than As, 3. less strongly than Si, 4. more strongly than S.</p>	<p>S and O. $[O^{1/2}, S^{1/4}] = 18,000.$ Is not decomposed by passing through a red hot tube, but by heating to c. 1200° C it changes to S + SO_3. Is reduced by red hot C. K and Sb burn in SO_2. O attracts S 1. less strongly than P, 2. more strongly than Cl, 3. more strongly than Se.</p>	<p>O and Cl. $[O^{1/2}, Cl] = -9,000.$ All the oxides of Cl are unstable explosive bodies. O and Cl do not directly combine. O attracts Cl 1. more strongly than F, 2. more strongly than Br, 3. more strongly than S.</p>
<p>Cu and O. $[O^{1/2}, Cu] = 20,000.$ Easily reduced to Cu by H or C. O attracts Cu 1. less strongly than Ca, 2. more strongly than Ag, 3. less strongly than Zn.</p>	<p>Zn and O. $CO^{1/2}, Zn^{1/2}] = 42,700.$ ZnO is not decomposed at 1750° C. It is reduced to Zn by heating in CO or with C. O attracts Zn 1. more strongly than Cu, 2. more strongly than Ga? 3. less strongly than Mg, 4. more strongly than Cd.</p>	<p>Ga_2O_3. Can be reduced to Ga by H at a high temp°. Is stable at a white heat. O attracts Ga 1. less strongly than Al, 2. more strongly than In, 3. more strongly than Zn, 4. more strongly than Ge.</p>	<p>GeO_2. GeO_2 can be reduced to Ge by C or H at a red heat. Ge attracts O 1. less strongly than Si, 2. more strongly than Sn, 3. less strongly than Ga, 4. more strongly than As.</p>	<p>As_2O_3. $[O^{1/2}, As^{1/3}] = 26,000.$ Can be reduced to As by heating with C, S, P, H, Na, CO &c. O attracts As 1. less strongly than P, 2. less strongly than Sb, 3. less strongly than Ge, 4. more strongly than Se.</p>	<p>Se and O. $[O^{1/2}, Se^{1/4}] = 14,000.$ SeO_2 is reduced to Se by Hl even at 10° C. $SeO_2 \cdot H_2O$ is easily reduced to Se. O attracts Se 1. less strongly than S, 2. less strongly than Te? 3. less strongly than As, 4. more strongly than Bi.</p>	<p>O and Br. OBr_2 is unknown. All the oxygen compounds of Br are less stable than the corresponding oxygen compounds of Cl. O attracts Br 1. less strongly than Cl, 2. less strongly than I, 3. less strongly than Se.</p>
<p>Ag and O. $[O^{1/2}, Ag] = 2,900.$ Ag_2O are completely decomposed to Ag and O at 340° C. O attracts Ag 1. less strongly than Cu, 2. more strongly than Au, 3. much less strongly than Cd.</p>	<p>Cd and O. $[O^{1/2}, Cd^{1/2}] = 37,700.$ Stable at 1750° C. Is somewhat easier to reduce to Cd by C than is ZnO. O attracts Cd 1. less strongly than Zn, 2. more strongly than Hg, 3. much more strongly than Ag, 4. more strongly than In?</p>	<p>In_2O_3. Is stable at 1750° C. Is reduced to metal by heating with C, H, or Na. In H reduction begins at c. 190 to 200° C and at c. 300° C in O obtained. In_2O_3 is considerably easier to reduce to In than is Ga_2O_3. O attracts In 1. less strongly than Ga, 2. more strongly than Tl, 3. less strongly than Cd, 4. slightly more strongly than Sn?</p>	<p>SnO_2. SnO_2 suffers a slight loss of O at 1750° C. Can be reduced to Sn by heating to a red heat with H, C, Na, K &c. O attracts Sn 1. less strongly than Ge, 2. less strongly than In? 3. more strongly than Pb, 4. about same strength as Sb.</p>	<p>Sb_2O_3. $[O^{1/2}, Sb^{1/3}, O_3, 3H_2O] = 27,900$ Sb_2O_3 decompose to Sb_2O_3 at 1750° C. Sb_2O_3 itself seems stable at this temp°. Can be reduced by C. O attracts Sb 1. more strongly than As, 2. more strongly than Bi, 3. as strongly as Sn?</p>	<p>Te and O. $[Te, O_3, Aq] = 98,380;$ compare $[Se, O_3, Aq] = 76,6.$ TeO_2 is stable at a red heat. It is reduced to Te by heating with H or C. O attracts Te 1. less strongly than Sb, 2. more strongly than Se? 3. more strongly than I.</p>	<p>I_2O_5. $[O^{1/2}, I^{1/5}] = 9,000.$ Decomposes at 300° C into O and I. O attracts I 1. more strongly than Cl or Br, 2. more strongly than Te.</p>
<p>Au and O. Completely decomposed to Au at 250° C. O attracts Au 1. less strongly than Ag, 2. less strongly than Hg,</p>	<p>Hg_2O. $[O^{1/2}, Hg] = 12,400.$ Decomposed when strongly heated to Hg and O. O attracts Hg 1. less strongly than Cd, 2. more strongly than Au, 3. less strongly than Tl.</p>	<p>Tl and O. $[O^{1/2}, Tl] = 21,100.$ Tl_2O is reduced to Tl by heating to redness in H or CO. Tl_2O_3 at a dull red heat is decomposed to $Tl_2O + O$. Tl_2O is easier to reduce to Tl than is In_2O_3 to In. O attracts Tl 1. less strongly than In, 2. more strongly than Hg, 3. less strongly than Pb.</p>	<p>PbO. $[O^{1/2}, Pb^{1/2}] = 25,000.$ PbO is unchanged at 1750° C. PbO_2 readily evolves O when heated. PbO is reduced to Pb by H or CO at a little above 100° C. O attracts Pb 1. less strongly than Sn, 2. more strongly than Tl? 3. more strongly than Bi?</p>	<p>Bi_2O_3. $[O^{1/2}, Bi^{1/3}, O_3, 3H_2O] = 23,000.$ Is unchanged at 1750° C. Heated in CO reduction begins at 200° C; in H at 240° C. O attracts Bi 1. less strongly than Sb, 2. less strongly than Pb?</p>		



rises at O (O atoms combine together with a very considerable force as O₂ and O₃) then again becomes very small at F.

Li 19.2; Be 17; B 13.2; C 6; N 0.2; O 5; F 0.1.

Na, Mg, Al, Si, P, S, Cl. The attraction for O rises from Na to Mg, then falls gradually becoming very small at Cl.

Na 12.5; Mg 16.5; Al 14.7; Si 13.8; P 9.25; S 4.5; Cl 0.2.

Cu, Zn, Ga, Ge, As, Se, Br. The attraction for O rises rapidly from Cu to Zn, then falls slowly, becoming very small at Br.

Cu 5; Zn 10.6; Ga 10; Ge 9.3; As 6.5; Se 3.5; Br 0.1.

Ag, Cd, In, Sn, Sb, Te, I. The attraction for O is very small for Ag, rises rapidly from Ag to Cd, falls slowly thence to I.

Ag 0.6; Cd 9.4; In 9.5; Sn 8; Sb 7.5; Te 3.0; I 2.5.

Au, Hg, Tl, Pb, Bi. The attraction for O is very small for Au and rises thence to Bi. Where the affinity is considerable.

Au 0.5; Hg 3.1; Tl 5.2; Pb 6.25; Bi 7.4.

Longitudinal Sections.

H, Li, Na, Cu, Ag, Au. The attraction for O rises from H to Li, then falls gradually, being small for Au.

H 8.5; Li 19.2; Na 12.5; Cu 5.0; Ag 0.6; Au 0.5.

Be, Mg, Zn, Cd, Hg. The attraction for O rises very slightly from Be to Mg, then steadily falls, being small at Hg.

Be 17; Mg 16.5; Zn 10.6; Cd 9.4; Hg 3.1.

B, Al, Ga, In, Tl. The attraction for O rises very considerably from Be to Al, and then falls slowly to Tl.

B 13.2; Al 15.7; Ga 10.0; In 9.5; Tl 5.2.

C, Si, Ge, Sn, Pb. The attraction for O rises very considerably from C to Si, then falls slowly to Pb.

C 6.0; Si 13.8; G 9.3; Sn 8.0; Pb 6.25.

N, P, As, Sb, Bi. The attraction is very small for N, suddenly and rapidly rises up to B, falls for As, again rises somewhat at Sb, and falls very slightly at Bi.

N 0.2; P 9.25; As 6.5; Sb 7.5; Bi 7.4.

O, S, Se, Te. The attraction for O rises very slightly from O to S, falls somewhat for Se, rises again for Te.

O 5.0; S 4.5; Se 3.5; Te 3.0.

F, Cl, Br, I. The attraction for O is very small for all these elements, rising from F to Cl, sinking somewhat from Cl to Br, and again rising from Br to I, where it attains its greatest value.

F 0.1; Cl 0.2; Br 0.1; I 2.5.

Fluorine

Longitudinal Sections.

H, Li, Na, Cu, Ag, Au. The attraction for F is great at H, rises to Li, sinks somewhat from Li to N, a large drop occurs as we pass from Na to Cu, the affinity continually diminishing until Au is reached.

H 9.65; Li 28; Na 27; Cu 4.5; Ag 3; Au 0.2.

Be, Mg, Zn, Cd, Hg. The affinity for F is great at Be, seems to increase slightly as we pass to Mg, then falls steadily until Hg is reached.

Be 21.25; Mg 24.25; Zn 13; Cd 12; Hg 3.

B, Al, Ga, In, Tl. The affinity is great for B, seems to rise at Al, then falls until Tl is reached.

B 14.5; Al 20.5; C 11; In 10; Tl 6.

C, Si, Ge, Sn, Pb. The affinity is considerable at C, rises as we pass from C to Si, then seems to fall slowly until Pb is reached remaining, however, still considerable at Pb.

C 5.7; Si 16.8; Ge 10; Sn 9.0, Pb 8.0.

N, P, As, Sb, Bi. The affinity is very small for N, rises for P, then seems to sink somewhat for As, and then increases somewhat as we pass in succession to Sb and Bi.

N 0.1; P 8.8; As 8.5; Sb 8.7; Bi 8.9.

O, S, Se, Te. The affinity for F is very small at O, is great at S, seems to fall somewhat at Se, and then rise somewhat at Te.

O 0.1; S 4.5; Se 4.0; Te 5.

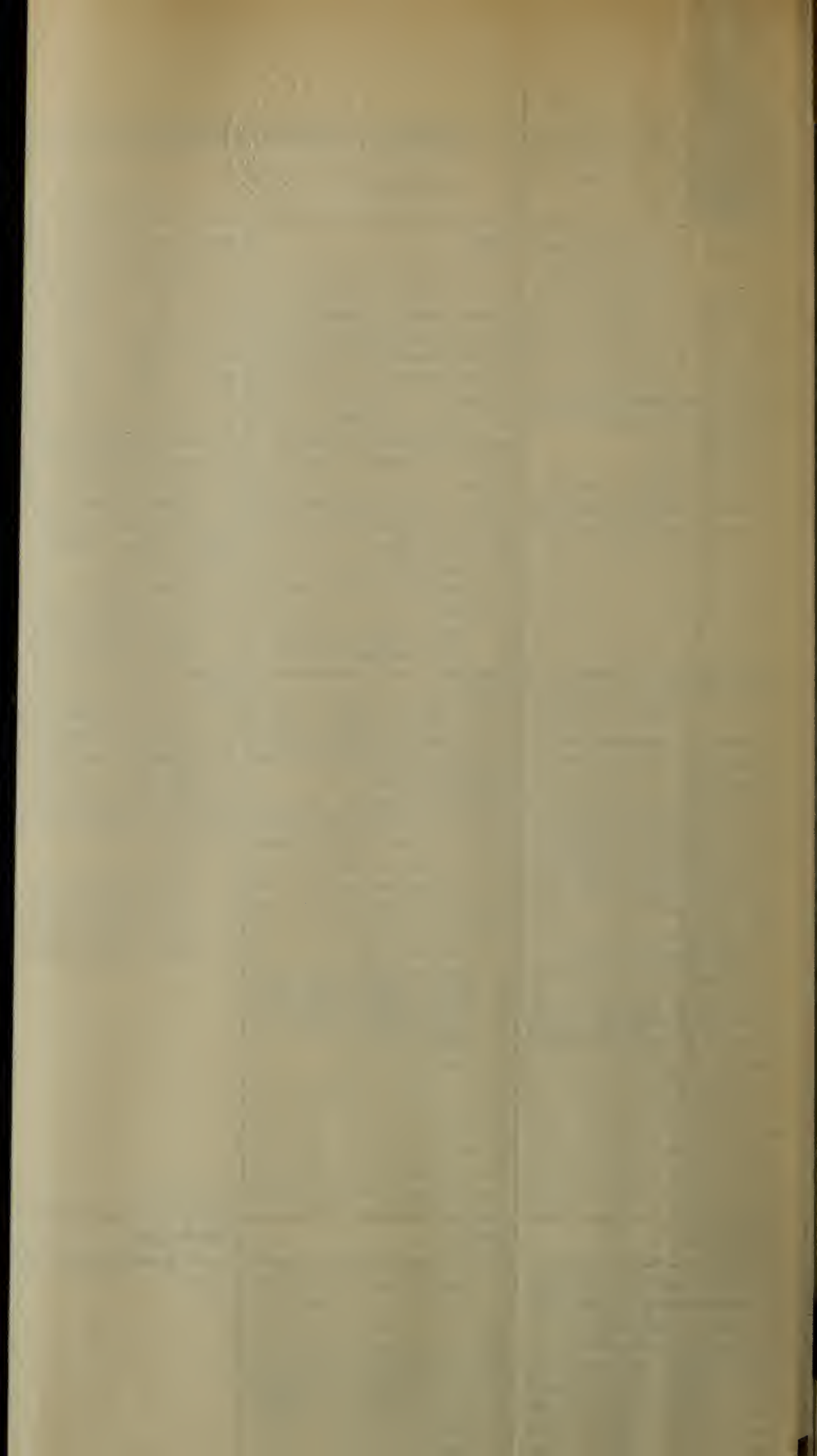
F, Cl, Br, I. F atoms seem to attract each other strongly, chlorine has but a feeble affinity for F, and the attraction steadily increases as we proceed towards I.

F 5; Cl 0.2; Br 1.0; I 4.5.

H and F. $[F, H] = 38,600$.
H and F explode together at ordinary temperatures to produce HF. HF seems a very stable body.

Data for determining the intensity of the force with which the various elements of the primary system A attract Fluorine.

<p>Li and F. $[Li, F]$ probably about 112,000?</p> <p>LiF is easily decomposed by HNO_3 or H_2SO_4, but with difficulty by aqueous HCl. At a red heat it is completely decomposed by HCl and partially by steam. Partially volatilises at 1100 to 1200°C.</p> <p>F attracts Li</p> <ol style="list-style-type: none"> 1. more strongly than H, 2. more strongly than Na? 3. more strongly than Be? 	<p>BeF₂. $[Be^{1/2}, F]$ about 85,000?</p> <p>Be when brought into contact with F rapidly becomes incandescent, and is transformed into a fluoride which in part is volatilised. BeF₂ is completely fluid at 800°C. Heated in O it goes into an oxy-fluoride. But S vapour has no action on it. It is decomposed by H_2SO_4, and also by heating to redness with K, Na or Mg.</p> <p>Be attracts F</p> <ol style="list-style-type: none"> 1. probably less strongly than Li, 2. less strongly than Mg? 3. more strongly than B. 	<p>BF₃. $[B^{1/3}, F]$ about 58,000?</p> <p>Formed by heating B in F; or by heating $B_2O_3 + CaF_2$ at a white heat. Colourless gas. Suffocating odour. Acts on organic matter like conc. H_2SO_4. Incombustible. Not decomposed by electric sparks. Does not act on glass. Is very stable. Not decomposed by Fe at a red heat. Alkali and alkali earth metals at a red heat liberate B. With water forms $HF.BF_3$ and $HBO_2.HF$.</p> <p>F attracts B</p> <ol style="list-style-type: none"> 1. less strongly than Be, 2. less strongly than Al, 3. more strongly than C. 	<p>CF₄. $[C^{1/4}, F] < [C^{1/4}, O^{1/2}] < 24,200$ $> [C^{1/4}, Cl] > 13,500$</p> <p>probably about 23,000.</p> <p>F and C combine with great energy at ordinary temps⁰ evolving heat and light. Below a red heat CF₄ is formed. Above a red heat C₂F₂ seems to be formed. Both fluorides when heated decompose and polymerise. CF₄ is decomposed by glass or by alcoholic KOH. C₂F₄ is the most stable fluoride. Not decomposed by electric sparks.</p> <p>F attracts C</p> <ol style="list-style-type: none"> 1. less strongly than B, 2. more strongly than N, 3. less strongly than Si. 	<p>NF₃.</p> <p>Unknown and certainly less stable than NCl₃ since it cannot be produced by methods analogous to those which produce NCl₃.</p>	<p>O and F.</p> <p>No compound of O and F is known. F seems to be quite inert towards O and cannot be made to combine with it.</p> <p>O and F have no affinity for each other.</p>	<p>F and F.</p> <p>The molecules F₂ seem capable of existing stably at ordinary temps⁰. Moissan has recently shown that the vapour density of F gas corresponds to the mol. wt. F₂. Hence fluorine atoms seem to possess a considerable attraction for each other.</p>
<p>Na and F. $[Na, F]$ probably about 110,000?</p> <p>Na and F combine directly together. NaF melts at a high temp⁰; decomposed by heating to redness in H₂O vapour, with formation of NaOH and HF. Completely decomposed to NaCl by heating strongly in HCl gas. Also by heating strongly with NH₄Cl.</p> <p>F attracts Na</p> <ol style="list-style-type: none"> 1. a little less strongly than Li, 2. more strongly than Cu, 3. more strongly than Mg? 	<p>MgF₂. $[Mg^{1/2}, F]$ about 97,000?</p> <p>Mg powder when heated in F gas to a dull red heat burns brilliantly.</p> <p>White tasteless powder; insol. in acids and water. Melts at the fusing point of cast iron; does not seem to be acted on by O — at least no mention is made whether it is or not.</p> <p>F attracts Mg</p> <ol style="list-style-type: none"> 1. more strongly than Be? 2. less strongly than Na, 3. more strongly than Zn, 4. more strongly than Al. 	<p>AlF₃. $[Al^{1/3}, F]$ about 82,000?</p> <p>Very stable body. Can be obtained by action of HF on Al₂O₃. Unacted on by air or acids or by aqueous alkalis. Volatile at a bright red heat.</p> <p>F attracts Al</p> <ol style="list-style-type: none"> 1. more strongly than B? 2. less strongly than Mg? 3. more strongly than Si? 4. more strongly than Ga. 	<p>SiF₄. $[Si^{1/4}, F] = 67,300$.</p> <p>Formed by passing BF₃ vapour thro' a red hot porcelain tube. Also by action of HF on SiO₂. Gas. Is decomposed by electric sparks with separation of Si. K and Fe when hot burn in the gas forming fluorides and Si. Moist air forms Si₂O₅.F.OH. Water decomposes SiF₄ forming SiO₂.XH₂O and H₂SiF₆.</p> <p>F attracts Si</p> <ol style="list-style-type: none"> 1. more strongly than C, 2. less strongly than Al, 3. more strongly than Ge, 4. more strongly than P. 	<p>P and F. $[P^{1/5}, F]$ probably about 35?</p> <p>PF₃. Gas. Decomposed by hot Si to form SiF₄. Decomposed by heat. In a glass apparatus P + SiF₄ is formed. Very slowly decomposed by H₂O, forming H₃PO₃ + HF. More rapidly decomposed by steam at 100°C.</p> <p>Decomposed by KOH.Aq.</p> <p>PF₅. Gas. Not acted on by S vapour at 440°C. Hence P attracts F more strongly than S. Decomposed by powerful electric sparks but not by ordinary sparks.</p> <p>F attracts P</p> <ol style="list-style-type: none"> 1. much more strongly than N, 2. more strongly than As, 3. less strongly than Si, 4. more strongly than S. 	<p>S and F.</p> <p>S when brought into contact with F burns vividly, producing SF₆ and lower fluorides.</p> <p>SF₆ is a very stable gas. Incombustible. Does not support combustion. P, B, Si, Ag, Cu when heated in it to a red heat do not decompose it. KOH does not act on it. Not changed when heated up to the melting point of hard glass. At the temp⁰ of the electric spark it is partially decomposed. The lower fluorides are less stable, acting on glass to produce SO₂ + SiF₄.</p> <p>F attracts S</p> <ol style="list-style-type: none"> 1. much more strongly than O, 2. more strongly than P? 3. more strongly than Cl. 	<p>Cl and F.</p> <p>F when brought into contact with Cl does not combine with it, at least at ordinary temps⁰. Cl seems to have but a feeble affinity for F, much smaller than Br or I have.</p> <p>F attracts Cl</p> <ol style="list-style-type: none"> 1. less strongly than F, 2. less strongly than Br, 3. less strongly than S.
<p>Cu and F.</p> <p>CuF₂. Heated to 300°C in air, CuO is formed. Heated in steam gives CuO + HF. CuF₂.2H₂O decomposes spontaneously in 4-5 days to oxy-fluorides and evolves HF. Heated above 500°C CuF₂ decomposes to Cu₂F₂. HCl forms CuCl₂.CuF₂. H₂S forms CuS + HF.</p> <p>Cu₂F₂. Red powder. Decomposed by moist air to Cu(OH)₂.CuF₂. It is easily reduced by H at a red heat. Cu has in fact but a feeble affinity for F.</p> <p>F attracts Cu</p> <ol style="list-style-type: none"> 1. less strongly than Na, 2. more strongly than Ag, 3. less strongly than Zn. 	<p>ZnF₂.</p> <p>Zn when gently warmed in F gas inflames brilliantly. Is formed by the action of dry HF on ZnCl₂ at 800 to 900°C. Also by action of HF on ZnO at a red heat. Also on Zn. When heated in air or to redness in steam is wholly changed to ZnO. Heated with H₂S forms ZnS and with HCl forms ZnCl₂. Reduced by H at a red heat.</p> <p>F attracts Zn</p> <ol style="list-style-type: none"> 1. less strongly than Mg, 2. more strongly than Cu, 3. more strongly than Cd. 	<p>Ga and F.</p> <p>No fluoride been investigated.</p>	<p>Ge and F.</p> <p>Pure GeF₄ has not yet been obtained. GeF₄.3H₂O however is known. When heated HF and H₂O are evolved and some GeO₂ is formed. Heated to redness GeF₄ is evolved and about half the Ge remains as GeO₂. O acts on GeF₄ decomposing it.</p> <p>F attracts Ge</p> <ol style="list-style-type: none"> 1. less strongly than Si, 2. more strongly than Sn, 3. less strongly than Ga, 4. more strongly than As. 	<p>As and F.</p> <p>As inflames in F to produce AsF₃ and traces of AsF₅. AsF₃ is a limpid liquid, decomposed by H₂O to As₂O₃ + HF. It acts slowly on glass.</p> <p>F attracts As</p> <ol style="list-style-type: none"> 1. less strongly than P, 2. less strongly than Ge, 3. less strongly than Sb. 	<p>Se and F.</p> <p>Se when brought into contact with F, first produces white fumes, then glows and takes fire. Around the Se there condenses a white compound which is decomposed by H₂O.</p> <p>F attracts Se</p> <ol style="list-style-type: none"> 1. less strongly than As, 2. less strongly than S, 3. more strongly than Br. 	<p>Br and F.</p> <p>According to Moissan, F brought into contact with Br vapour, combines with the production of a flame. Brought into contact with liquid Br it also combines, but the reaction is not accompanied by a flame. But little heat seems to be evolved in this reaction.</p> <p>F attracts Br</p> <ol style="list-style-type: none"> 1. more strongly than Cl, 2. less strongly than I, 3. less strongly than Se.
<p>Ag and F.</p> <p>AgF is a yellow solid, melts at about 435°C. When AgF.2H₂O is dried in vacuo some oxy-fluoride is always formed. Heated in air AgF is decomposed by the moisture present to Ag, O, and HF. AgF reacts violently with POCl₃, PCl₅, SiCl₄, BCl₃, giving AgCl and fluoride of P, Si, or B. Heated with I produces AgI. Ag has a feeble affinity for F, certainly a smaller affinity than for Cl.</p> <p>F attracts Ag</p> <ol style="list-style-type: none"> 1. less strongly than Cu, 2. more strongly than Au, 3. less strongly than Cd. 	<p>CdF₂.</p> <p>CdF₂ can be obtained by precisely the same methods as ZnF₂, but at lower temps⁰. It corresponds to ZnF₂ in properties, being decomposed when heated in air or to redness in steam with production of ZnO.</p> <p>F attracts Cd</p> <ol style="list-style-type: none"> 1. less strongly than Zn, 2. more strongly than Ag, 3. more strongly than Hg. 	<p>In and F.</p> <p>No fluoride yet been investigated.</p>	<p>Sn and F.</p> <p>SnF₄ formed by SnO. xH₂O + HF.Aq. Heated in air forms the oxy-fluorides. SnF₄ has not been isolated. A soln. of SnO₂.xH₂O in HF.Aq coagulates when heated, but does not yield any definite compound. When evaporated in air oxy-fluorides are formed and HF is given off. Sn combines but slowly with F in the cold. Warmed to 100°C, however, it becomes incandescent and evolves a large amount of heat.</p> <p>F attracts Sn</p> <ol style="list-style-type: none"> 1. less strongly than Ge, 2. more strongly than Pb, 3. more strongly than Sb. 	<p>Sb and F.</p> <p>SbF₃ formed Sb₂O₃ + HF. White body. Sol. in H₂O without decomposition (∴ more stable than SbCl₃). Soln. in H₂O yields on evaporation an oxy-fluoride. SbF₅ is a gum-like mass. Decomposed by heat. Very slowly decomposed in solution by H₂S. According to Moissan, Sb inflames in F at ordinary temps⁰ producing a white solid fluoride.</p> <p>F attracts Sb</p> <ol style="list-style-type: none"> 1. less strongly than As? 2. less strongly than Sn? 3. less strongly Bi? 	<p>Te and F.</p> <p>Only TeF₄ known. Produced H₂TeO₃ + HF. According to Moissan, powdered Te combines with F gas, becoming incandescent and producing a white easily volatile fluoride.</p> <p>F probably attracts Te</p> <ol style="list-style-type: none"> 1. more strongly than Se? 2. less strongly than Sb? 3. more strongly than I? 	<p>I and F.</p> <p>I and F combine together with the evolution of much heat and the production of a flame to produce IF₅. This is a colourless liquid, which is decomposed by H₂O to form HIO₃ and HF. Attacks glass and Si at a red heat.</p> <p>F attracts I</p> <ol style="list-style-type: none"> 1. more strongly than Br, 2. less strongly than Te.
<p>Au and F.</p> <p>Gold has very little affinity for F. Moissan states that Au reacts on F at a dull red heat to produce a yellow substance, which is volatile and decomposes at a temp⁰ a very little above that at which it is formed into Au and F. Lenher (1903) proves that HF will not decompose gold oxide; nor can it be produced by action of AgF on AuCl₃. AuF₃ is, in fact, a very unstable substance.</p> <p>Au attracts F</p> <ol style="list-style-type: none"> 1. less strongly than Ag, 2. less stable than Hg. 	<p>Hg and F.</p> <p>HgF. Unstable body. Decomposed to Hg and F when heated above 200°C. Decomposed by H₂O to HF and HgO. Also decomposed by alkalis with separation of Hg₂O.</p> <p>HgF₂. The hydrated fluoride HgF₂.2H₂O is decomposed at 30°, giving H₂O, HF and oxy-fluorides. HgF₂ is decomposed by water with separation of H₂O.</p> <p>Hg seems to have a quite feeble affinity for F, certainly a smaller affinity than for Cl.</p> <p>F attracts Hg</p> <ol style="list-style-type: none"> 1. less strongly than Cd, 2. more strongly than Au, 3. less strongly than Tl. 	<p>Tl and F.</p> <p>Thallium burns when placed in F, producing TlF₃. TlF₃ is easily fused. Melts to orange liquid which becomes white on cooling. Is insol. in cold H₂O and cold HCl.Aq.</p> <p>TlF. Can be formed as a white sublimate by heating Tl₂O in HF. Prepared Tl₂CO₃ + HF + Aq.</p> <p>Tl attracts F</p> <ol style="list-style-type: none"> 1. probably less strongly than Ga? 2. more strongly than Hg, 3. less strongly than Pb? 	<p>PbF₂.</p> <p>Pb when heated in F gas slowly combines with it. In 24 hours combination is complete. It heated gently Pb becomes incandescent producing PbF₂. HF does not act on Pb. White insol. body. Dissolves in HNO₃. NH₃.Aq produces an oxy-fluoride.</p> <p>F attracts Pb</p> <ol style="list-style-type: none"> 1. more strongly than Tl, 2. less strongly than Sn, 3. less strongly than Bi. 	<p>Bi and F.</p> <p>Only BiF₃ is known. Prod. Bi₂O₃ + HF. Stable body. Unacted on by H₂O. Scarcely changed or volatilised by heating to redness in an open Pt dish. Not oxidised by heating in nitrous oxides. Dissolved without decomposition by hot HCl, HNO₃ or H₂SO₄.</p> <p>According to Moissan. Bi does not combine with F in the cold. At a red heat it is attacked superficially only.</p> <p>F attracts Bi</p> <ol style="list-style-type: none"> 1. more strongly than Sb, 2. perhaps more strongly than Sn. 		

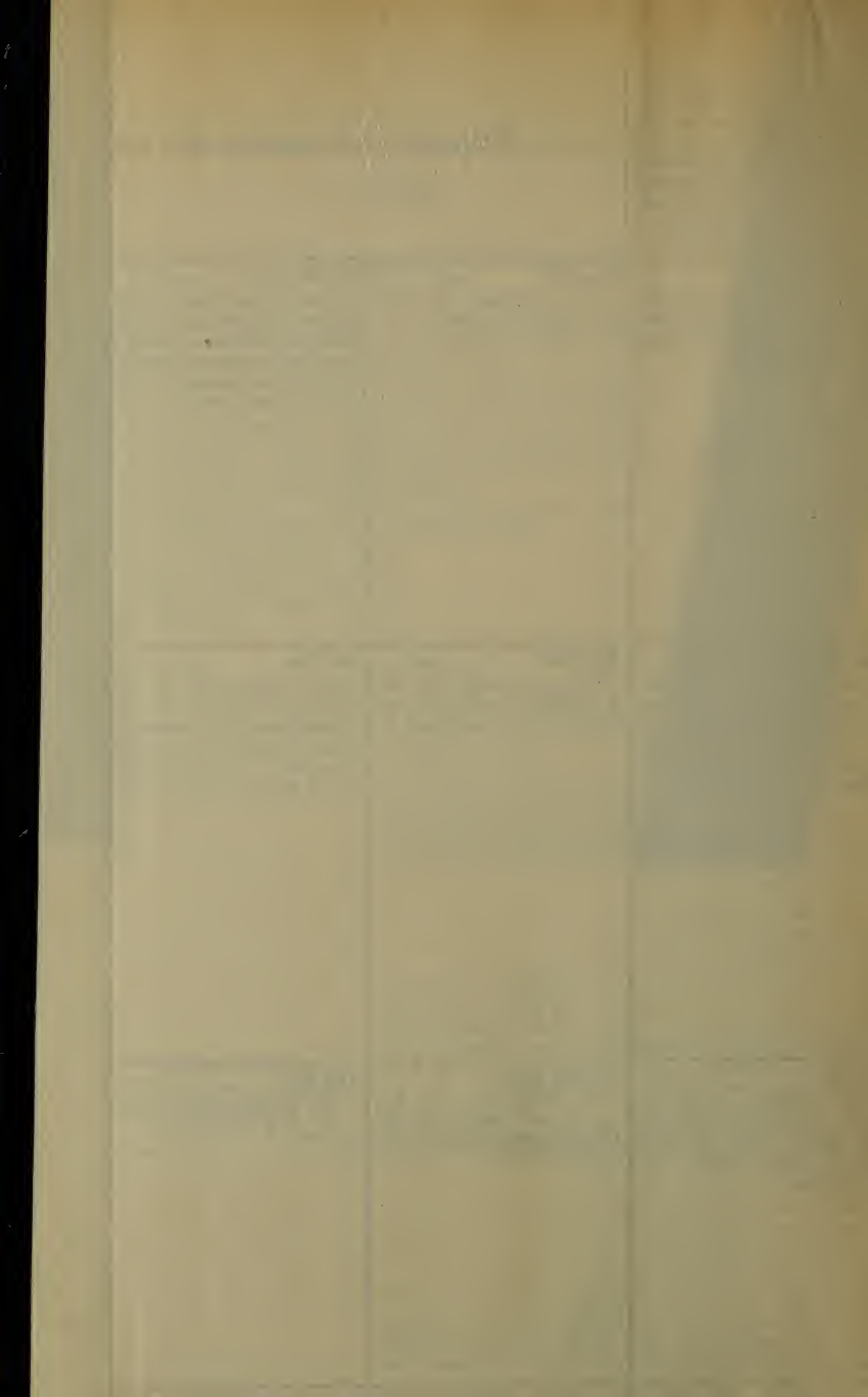


HNa_2 [H, Na] = 13,000.

Na_2H can be melted without decomposition in H. Heated in vacuo a regular dissociation takes place from 330° to 430° . Na_2H appears to be slightly more stable than K_2H . Na has but a feeble attraction for H.

Data for determining the force with which the various elements of the primarysystem A attract Sodium.

<p>Na, Li.</p> <p>No compound seems known. Na and Li have only a very feeble affinity for each other.</p>	<p>Be, Na.</p> <p>No compound or alloy has been described.</p>	<p>B, Na.</p> <p>No boride of Na has been obtained neither has a silicate (Na and Si do not directly unite when heated together.) Hence the affinity of Na for B seems small.</p>	<p>C_2Na_2. [Na, C] = 1,480.</p> <p>White solid. Not sensitive to shock or friction; very chemically active; more so than CaC_2; cannot be obtained in the electric furnace because it decomposes to Na and C at temps considerably lower than that of the arc. Dissociates into C and Na when heated to redness in a vacuum. Violently decomposed by H_2O evolving C_2H_2. NaC is less stable than LiC, MgC_2 and CaC_2. Na, in fact, attracts C with only a feeble force.</p>	<p>N, Na.</p> <p>No definite nitride Na_3N has been prepared. N does not directly combine with Na, even at a very high temp. NaNH_2 when heated to 500°C decomposes to Na, N, H; the K compound is somewhat more stable. NaN_3 and KN_3 are known.</p> <p>N has in fact but a feeble affinity for Na.</p>	<p>ONa_2 [$\text{Na}, \text{O}^{1/2}$] = 45,500.</p> <p>Na takes fire when gently warmed in air, and burns forming an oxide.</p> <p>Na attracts O</p> <ol style="list-style-type: none"> 1) much more strongly than N, 2) less strongly than F, 3) more strongly than S 	<p>F, Na.</p> <p>F and Na combine directly together. NaF melts at a high temp. without decomposition. Partially decomposed by heating to redness in H_2O vapour, with formation of NaOH and HF. Completely decomposed by heating strongly in HCl gas. Also by heating with NH_4Cl.</p> <p>N attracts F</p> <ol style="list-style-type: none"> 1) more strongly than O 2) less strongly than Cl.
<p>Na and Na.</p> <p>The molecule of Na seems to be mon-atomic, both as vapour and when dissolved in Hg. Hence Na atoms seem to have but a feeble affinity for each other.</p>	<p>Mg, Na.</p> <p>Mg alloys with Na, but no definite compound seems to have been described.</p>	<p>Al, Na.</p> <p>Na alloys with Al and the alloy thus formed easily decomposes H_2O. No definite compound has been described. Al in fact has but in feeble affinity for Na.</p>	<p>Si, Na.</p> <p>Si and Na do not combine directly when heated together. Na seems to have but a feeble affinity for Si.</p>	<p>PNa_3.</p> <p>Na and P combine with the evolution of much heat by merely adding P to Na under rock oil.</p> <p>Na_3P, a black solid, may be kept in dry air; in moist air, water or acids, it gives off inflammable PH_3. Na seems to have a considerable affinity for P.</p> <p>Na attracts P</p> <ol style="list-style-type: none"> 1) more strongly than N, 2) " " " Si. 	<p>S, Na.</p> <p>Na and S combine together with the evolution of heat and light. Several compounds are known, eg Na_2S, Na_2S_2.</p> <p>Na attracts S</p> <ol style="list-style-type: none"> 1) with a greater force than O? (see Na and also K), 2) less strongly than Cl. 	<p>Cl, Na. [Na, Cl] 97,709.</p> <p>Na burns in moist Cl to form NaCl; melts and vaporises at a high temp. not decomposed by superheated steam or by heating in air.</p> <p>Not decomposed by H or O at a red heat. H_2S converts it into Na_2S partially. Hence Na seems to have a greater attraction for S than for O, since O or H_2O cannot bring about this result.</p> <p>Na attracts Cl</p> <ol style="list-style-type: none"> 1) more strongly than Se, 2) " " " Br, 3) " " " S.
<p>Cu, Na.</p> <p>No definite compound seems to have been isolated. Cu and Na seem to have only a feeble affinity for each other.</p>	<p>Zn and Na.</p> <p>Zn alloys with Na, but no definite compound has been described. affinity very feeble.</p>	<p>Ga, Na.</p> <p>No compound seems to have been described.</p>	<p>Ge, Na.</p> <p>No combination or alloy with Na seems to have been described.</p>	<p>As, Na.</p> <p>Na and As combine directly together when heated with the evolution of much heat. The heat is so great that a large part of the metal or of the As is volatilised before the reaction is complete.</p> <p>Lebeau prepares Na_3P by heating $\text{Na} + \text{P}$ and dissolving out excess of Na with liquid NH_3. Is decomposed by H_2O giving AsH_3.</p>	<p>Se, Na.</p> <p>Na and Se combine directly together when warmed to form various compounds eg Na_2Se and Na_2Se_2.</p> <p>Na_2Se IO H_2O consists of white needles, which rapidly turn red and then brown and become coated with grey Se. It evolves H_2Se on exposure to air or when treated with dilute acids, melts to a brown liquid when warmed.</p>	<p>Br, Na. [Br, Na] = 85,770.</p> <p>Cl reacts with NaBr giving NaCl + Br.</p> <p>Na attracts Br</p> <ol style="list-style-type: none"> 1) more strongly than Se 2) " " " Cl 2) " " " I
<p>Ag and Na.</p> <p>Silver alloys with Na, but no definite compounds seem to have been separated. The affinity of Ag for Na is small.</p>	<p>Cd, Na.</p> <p>Cd alloys with Na, and a definite compound Cd_2Na has been described. The affinity of Na for Cd seems greater than its affinity for Zn.</p>	<p>In, Na.</p> <p>No compound seems to have been described.</p>	<p>Sn, Na.</p> <p>Na alloys with Sn, and a definite compound Na_3Sn has been obtained. This alloy is decomposed by H_2O. Na seems to have but a feeble affinity for Sn.</p>	<p>Sb, Na.</p> <p>Na and Sb combine directly together when heated to form Na_3Sb. Sb and Na seem to have a considerable affinity for each other.</p>	<p>Te, Na.</p> <p>Te and Na combine directly together with readiness.</p>	<p>I, Na. [I, Na] = 69,080.</p> <p>When Na and I are fused only very small quantities combine together. Heated in air some I is separated and O is absorbed, and the reaction becomes alkaline. Hence NaI is considerably less stable than NaBr or NaCl.</p> <p>Na attracts I</p> <ol style="list-style-type: none"> 1) less strongly than Br 2) more strongly than O.
<p>Au, Na.</p> <p>Au dissolves Na, but no definite compound seems to have been isolated. The affinity of Na for Au seems small.</p>	<p>Hg, Na. [Na, Hg] = 10,500. [Na, Hg] = 21,600.</p> <p>Na combines with Hg with the evolution of much heat and a number of definite compounds are formed. Na and Hg have therefore a considerable affinity for each other.</p>	<p>Tl, Na.</p> <p>Na alloys with Tl, but no definite compound seems to have been obtained.</p>	<p>Pb, Na.</p> <p>Pb alloys with Na and a definite compound, Na_3Pb has been obtained. The alloy may be formed by directly heating the elements together.</p> <p>Pb has a perceptible affinity for Na.</p>	<p>Bi, Na.</p> <p>Bi and Na combine directly together when heated, to form BiNa_3. Bi and Na seem to have a considerable affinity for each other.</p>		



Cross Sections.

Li, Be, B, C, N, O, F. The attraction for F is very great at Li and sinks gradually as we go towards O, being very small here, at F it seems to rise again.

H 9.65; Li 28; Be 21.25; B 14.5; C 5.7; N 0.1; O 0.1; F 5.

Na, Mg, Al, Si, P, S, Cl. The attraction for F is very great at F, then sinks slowly until Cl is reached, being very small here.

Na 27; Mg 24.25; Al 20.5; Si 16.8; P 8.8; S 4.5; Cl 0.2.

Cu, Zn, Ga, Ge, As, Se, Br. Copper has a comparatively feeble affinity for F, the attraction increases greatly as we go from Cu to Zn; then seems to sink gradually until Br is reached. Br has but a feeble affinity for F.

Cu 4.5; Zn 13; Ga 11; Ge 10; As 8.5; Se 4; Br 1.

Ag, Cd, In, Sn, Sb, Te, I. Ag has but a feeble affinity for F, the affinity increasing and probably attaining a maximum at In. Thence it sinks slowly to I.

Ag 3; Cd 12; In 10; Sn 9; Sb 8.7; Te 5.0; I 4.5.

Au, Hg, Tl, Pb, Bi. Gold has a very small affinity for F, the affinity rises as we pass down the series of elements, becoming greatest at Bi.

Au 0.2; Hg 3.0; Tl 6.0; Pb 8.0; Bi 8.9.

S o d i u m

Longitudinal sections.

F, Cl, Br, I. The attraction for Na is very great for all these elements decreasing as we pass from F to I.

F 27.0; Cl 24.4; Br 21.4; I 17.3.

O, S, Se, Te. The attraction for Na seems to rise somewhat as we pass from O to S; judging from thermal data Se exerts a stronger attraction than O.

O 11.4; S 13.0; Se 11.4; Te 9.0

N, P, As, Sb, Bi. The attraction of N for Na is feeble. P attracts it with a greater force and probably As with a force greater than P. Sb and Bi also combine readily with Na.

N 0.5; P 4.5; As 5.0; Sb 2.5; Bi 2.0.

C, Si, Ge, Sn, Pb. These elements have all but a very feeble affinity for Na.

C 0.4; Si 0.3; Ge 0.3; Sn 0.3; Pb 2.0.

B, Al, Ga, In, Tl. All seem to have an affinity for Na, Tl, however, readily alloys with Na.

B 2.5; Al 1.0; Ga 0.3; In 0.3; Tl 2.0.

Be, Mg, Zn, Cd, Hg. All seem to have an affinity for Na, Hg having the greatest — combining with Na with the evolution of much heat.

B 0.5; Mg 0.5; Zn 0.5; Cd 0.5; Hg 5.4.

H, Li, Na, Cu, Ag, Au. All seem to have only a very feeble affinity for Na.

H 3.25; Li 0.5; Na 0.5; Cu 0.5; Ag 0.5; Au 0.5.

Cross Sections.

Li, Be, B, C, N, O, F, Ne. So far as can be judged the attraction for Na remains small up to N, it then rises rapidly, being great for O and still greater for F.

Li 0.5; Be 1.0; B 2.5; C 0.5; N 0.4; O 11.4; F 27.4.

Na, Mg, Al, P, S, Cl, Ar. The attraction is small for Na and rises steadily until Cl is reached.

Na 0.5; Mg 1.0; Al 1.0; P 4.5; S 13.0; Cl 24.4.

Cu, Zn, Ga, Ge, As, Se, Br. The attraction is small for Cu and rises steadily until Br is reached.

Cu 0.5; Zn 0.5; Ga 0.3; Ge 0.3; As 5.0; Se 11.4; Br 21.4,

Ag, Cd, In, Sn, Sb, Te, I. The affinity rises steadily from Ag to I.

Ag 0.5; Cd 0.5; In 0.3; Sn 0.3; Sb 2.5; Te 9.0; I 17.3.

Au, Hg, Tl, Pb, Bi. The affinity for Na is small for Au, great for Hg, and decreases as we pass from Hg to Bi.

Au 0.5; Hg 5.4; Tl 2.0; Pb 2.0; Bi 2.0.

M a g n e s i u m

Cross Sections.

Li, Be, B, C, N, O, F. Li has but a very feeble affinity for Mg. The affinity rises as we pass from Li to F, very slowly at first, then rapidly after C is passed, attaining its greatest value at F.

Li 1.5; Be 1.0; B 2.5; C 3.5; N 4.0; O 16.5; F 22.0.

H and Mg.

A hydride was obtained by Winkler (1891) by heating MgO with Mg in a current of H. Decomposed by warm water evolving H. Heated in O burns with an H flame. Mg seems to attract H but feebly.

Data for determining the force with which the various elements of the primary system A attract Magnesium.

Li and Mg.

Mg + Li. No compound known. Probably but a feeble affinity. Mg however alloys with the alkali metals.

Be, Mg.

No compound seems to have been investigated.

B₂Mg₅?

Winkler (1890) showed, that when Mg + B₂O₃ is ignited, a brown mass, a mixture of Mg borate and boride is obtained. The boride Mg₂B₃ was oxidisable, attacked with difficulty by either water or alkalis, but dissolves easily and completely in HCl or NH₄Cl.

C and Mg.

MgC₂ is too unstable to be produced in the electric furnace, since it is decomposed in the arc from a current of 600 ampères and 60 volts. Can be produced mixed with C by heating Mg powder in a stream of C₂H₂. Decomposed by H₂O with evolution of gas. Mg has but a feeble affinity for C.

N and Mg.

Mg₃N₂ is formed by heating Mg in N, or by heating Mg + NH₃ together when a sudden glowing is observed. Is stable in N at a high temp^o; heated in air is slowly oxidised to MgO, oxidation is rapid in O. With H₂O forms MgO + NH₃. Heated in HCl get MgCl₂ + NH₄Cl. Mg attracts N
1. more strongly than C,
2. less strongly than O.

O and Mg.

[Mg^{1/2}, O^{1/2}] = 66,000. Mg burns in O brilliantly to form the very stable MgO.
Mg attracts O
1. more strongly than N,
2. less strongly than F?
3. more strongly than S.

F and Mg.

Mg powder when heated in F gas to a dull red heat, burns brilliantly to MgF₂. White tasteless powder; insol. in acids and water. Melts at the fusing point of cast iron. Mg probably attracts F
1. more strongly than O?
2. a little more strongly than Cl?

Na and Mg.

Mg alloys with Na, but no definite compound seems to have been described.

Mg and Mg.

Mg atoms seem to have but a feeble affinity for each other. Ramsay showed that the molecules of Mg dissolved in Hg consist of single Mg atoms.

Al and Mg.

Mg alloys with Al. Boudouard's researches (1901, 1902) show that definite compounds AlMg, AlMg₂, Al₃Mg probably exist. Mg, however, seems to have but a feeble affinity for Al.

Si and Mg.

Mg combines readily with Si when heated with it in the electric furnace. Also readily produced by heating Mg + SiO₂. Acted on by strong HCl evolving SiH₄. Water attacks it in the cold with the evolution of H. Since Mg + Si when heated together in a glass tube to a dull red heat combine with glowing, Mg has a considerable affinity for Si. Mg attracts Si
1. more strongly than C,
2. more than P.

P and Mg.

Solid. Can be obtained by heating P vapour and Mg in an atmosphere of H. Or by melting P + Mg in sealed tube. Readily decomposed by H₂O. Dry air or O is without action at ordinary temps^o, burns in O at a red heat. Also burns brilliantly when heated in Cl, Br, I. Acids decompose it, evolving PH₃. Mg attracts P
1. less strongly than N?
2. less strongly than S?
3. less strongly than Si?

S and Mg.

[Mg^{1/2}, S^{1/2}] = 19,900. MgS can be produced by heating Mg + S together. Also Mg + H₂S. H₂O decomposes amorphous MgS instantly to Mg(OH)₂ + H₂S. The crystalline sulphide is more stable. Readily oxidised when heated in O. Decomposed with incandescence when heated to 300^o C in Cl; also in Br and I. Not reduced by heating to a high temp^o with P, B, Si or Fe. Na, however, decomposes it. Amorphous MgS heated a few minutes in the electric furnace, fuses but remains undecomposed. Mg attracts S
1. less strongly than O.
2. more strongly than P,
3. less strongly than Cl,
4. more strongly than Se.

Cl and Mg.

[Mg^{1/2}, Cl] = 75,500. MgCl₂. Very stable body. Can be distilled in H at a red heat. When crystals of MgCl₂·6H₂O are heated in air, water is given off, and at the same time partial decomposition occurs with evolution of HCl and formation of oxy-chlorides. MgCl₂ is partially decomposed by much water to MgO + HCl. Mg attracts Cl
1. less strongly than F?
2. more strongly than Br,
3. more strongly than S.

Cu, Mg.

Alloys can be formed by adding Cu to Mg fused under NaCl. Boudouard describes 3 compounds CuMg₂, CuMg, Cu₂Mg. Mg has but a feeble affinity for Cu.

Zn and Mg.

Mg alloys with Zn, but no definite compound seems to have been isolated. Mg has but a feeble affinity for Zn.

Ga and Mg.

No alloy been described. Affinity but feeble.

Ge and Mg.

No alloys seem to have been investigated. Probably but a very feeble affinity exists.

As and Mg.

Mg heated suddenly with 5 or 6 times its weight of As, combines with explosion. Black brown powder. Mg has a perceptible affinity for As. Mg attracts As
1. less strongly than P,
2. more strongly than Sb,
3. more strongly than Se,
4. less strongly than Se.

Se and Mg.

A flesh coloured precipitate, probably a selenide of Mg is obtained by adding K₂Se to a soln. of Mg salt. The precipitate is decomposed by heat and by acids with separation of Se. Hence Mg seems to have but a feeble affinity for Se. Mg attracts Se
1. less strongly than S,
2. less strongly than Te,
3. more strongly than As.

Br and Mg.

[Mg^{1/2}, Br] = 65,850. MgBr₂ is obtained by passing Br vapour over molten Mg. Reaction is very violent. Evaporation of MgBr₂·aq to dryness, or heating the crystals of MgBr₂·2H₂O is attended with evolution of HBr and formation of an oxy-bromide. Heated in a stream of O, MgBr₂ is entirely decomposed to MgO. Mg attracts Br
1. less strongly than Cl,
2. more strongly than I,
3. more strongly than Se.

Ag, Mg.

Mg alloys with Ag, but no definite compound seems to have been described. Ag seems to have but a feeble affinity for Mg.

Cd and Mg.

Mg alloys with Cd. The experiments of Boudouard (1902) make probable the existence of 3 compounds CdMg, CdMg₂, CdMg₃₀; all alloys readily attacked in presence of H₂O. Mg seems to have but a feeble affinity for Cd.

In and Mg.

No alloy been described; affinity but feeble.

Sn and Mg.

Parkinson showed that Mg alloys with Sn. But no definite compound seems to have been obtained. Mg has probably but a feeble affinity for Sn.

Sb and Mg.

Alloys have been prepared, but no definite compound seems to have been described. Probably Mg has but a feeble affinity for Sb.

Te and Mg.

No compound seems to have been described.

I₂Mg.

[I, Mg^{1/2}] = 42,400. Obtained by throwing I in small quantities at a time on to molten Mg. The reaction is very violent. White solid. MgI₂ is decomposed by heating in air, giving off I and forming MgO. Heated in O it is entirely changed to MgO. Mg attracts I
1. less strongly than Br,
2. more strongly than Te.

Au and Mg.

Mg alloys with Au, but no definite compound has been prepared. Au seems to have but a feeble affinity for Mg.

Hg and Mg.

Mg alloys with Hg. Mg amalgams attack cold alcohol, forming Mg ethoxide and liberating H. Mg has but a feeble affinity for Hg.

Tl and Mg.

No alloy been described. Affinity feeble.

Pb and Mg.

Mg alloys with Pb, but no definite compound seems to have been described. Probably only a very feeble affinity exists between Pb and Mg.

Bi and Mg.

Bi alloys with Mg, but no definite compound seems to have been described. Bi has but a feeble affinity for Mg.

THE UNIVERSITY OF CHICAGO

PHYSICS DEPARTMENT

RESEARCH REPORT

NO. 100

1950

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Na, Mg, Al, Si, P, S, Cl. The affinity is feeble for Mg at Na, and rises as we pass towards Cl, attaining its greatest value at Cl.

Na 1; Mg 1; Al 2; Si 4; P 3.5; S 5; Cl 18.9.

Cu, Zn, Ga, Ge, As, Se, Br. The affinity for Mg is small at first, and rises as we pass from Cu towards Br, attaining its greatest value at Br.

Cu 0.8; Zn 1; Ga 1; Ge 3; As 3.4; Se 4.5; Br 16.5.

Ag, Cd, In, Sn, Sb, Te, I. The affinity is very feeble at first and rises as we pass towards I, becoming great at the latter element.

Ag 0.5; Cd 1; In 1; Sn 2.5; Sb 3; Te 3.8; I 10.6.

Au, Hg, Tl, Pb, Bi. The affinity is very feeble for all these bodies.

Au 0.4; Hg 0.5; Tl 0.8; Pb 1.0.

Longitudinal Sections.

H, Li, Na, Cu, Ag, Au. The affinity is extremely small for all these elements.

H 2.5; Li 1.5; Na 1; Cu 0.8; Ag 0.5; Au 0.4.

Be, Mg, Zn, Cd, Hg. For all these the affinity is very small

Be 1; Mg 1; Zn 1; Cd 1; Hg 0.5.

B, Al, Ga, In, Tl. The affinity seems to sink steadily from B to Tl and is very feeble for all these elements.

B 2.5; Al 2; Ga 1; In 1; Tl 0.8.

C, Si, Ge, Sn, Pb. C has but a feeble affinity for Mg. The affinity rises as we pass from C to Si and then probably falls until Pb is reached.

C 3.5; Si 4; Ge 3; Sn 2.5; Pb 1.

N, P, As, Sb, Bi. Nitrogen has a considerable affinity for Mg; So also have As and B. The affinity seems to fall steadily as we pass from N to Bi.

N 4; P 3.5; As 3.4; Sb 3; Bi 2.

O, S, Se, Te. The affinity is great for O, and rapidly sinks as we pass from O to Te.

O 16.5; S 5; Se 4.5; T 3.8.

F, Cl, Br, I. The attraction for Mg is probably somewhat greater in the case of F than for Cl, and sinks steadily as we pass from F to I. For all is the affinity for Mg very intense.

F 22; Cl 18.9; Br 16.5; I 10.6.

Aluminum.

Cross Sections.

Li, Be, B, C, N, O, F. The affinity for Al seems to sink somewhat as we pass from Li to B, being however, small for both these elements, it then rises rapidly as we pass from Be towards F, becoming very great at this latter element.

Li 2.5; Be 2.0; B 3.5; C 4.5; N 10.0; O 15.8; F 16.7.

Na, Mg, Al, Si, P, S, Cl. Up to Si the affinity for Al is feeble, it then rises, becoming considerable at P, great at S, and very great at Cl.

Na 2.0; Mg 1.9; Al 2; Si 3; P 5; S 8; Cl 13.4.

Ag, Cd, In, Sn, Sb, Te, I. The affinity for Al decreases as we pass from Ag to Cd, becoming very small at Cd. It then steadily increases attaining its greatest value at I.

Ag 1.6; Cd 0.3; In 1.5; Sn 2; Sb 3.5; Te 6; I 8.

Au, Hg, Tl, Pb, Bi. Au has an appreciable affinity for Al, Hg seems to have practically none. The alloys of the Tl, Pb, Bi are imperfectly known, but from analogy the affinity for Al probably rises as we pass from Hg to B.

Au 1.5; Hg 0.3; Tl 0.4; Pb 0.5; Bi 0.3.

Longitudinal Sections.

H, Li, Na, Cu, Ag, Au. The affinity is very small at H, and seems to rise as we pass from H to Li, and then slowly decreases as we pass towards Au, remaining, however, still perceptible at Au,

H 0.5; Li 2.5; Na 2.0; Cu 1.7; Ag 1.6; Au 1.5.

Be, Mg, Zn, Cd, Hg. No compound of Bi and Al seems to have been investigated. Mg has a considerable affinity for Al the affinity falls steadily as we pass from B to Hg, being very small at this latter point.

Be 2.0; Mg 1.9; Zn 0.5; Cd 0.4; Hg 0.3.

H and Al.

No hydride of Al is known, but is probably capable of existing.

Data for determining the force with which the various elements of the primary system A attract Aluminium.

Li and Al.

No alloy seems to have been described.

Be and Al.

No alloy been described.

Be and Al.

Can be made to combine by heating B or B_2O_3 + Al together to redness for about 2 hours. Also BCl_3 + Al when heated together. AlB is unchanged by heating in air. Slowly dissolves in conc. HCl (hot) and NaOH-Aq. Easily sol. in warm HNO_3 . AlB₆ consist of black crystals harder than corundum. Unacted on by conc. KOH or HCl. Oxidised by molten $KHSO_4$, not by KNO_3 .
Al attracts B probably less strongly than C.

C and Al.

C_3Al_4 prep'd. by heating Al + C, or C and clay in electric furnace 5-6 mins in a current of 300 amperes and 65 volts. Is decomposed at higher temps^o in the electric arc. Cl attacks it at dull red heat with incandescence. O only attacks it superficially at a dull red heat. S attacks it readily with great development of heat. Acids attack it usually very slowly. Fused KOH at 300^o attacks it with great energy. Decomposed slowly by H_2O forming CH_4 .

NAI.

Al combines with N when heated to very high temps^o. Is formed in the electric arc. Slowly decomposed by moist air to form $Al_2O_3 + H_2O$. Somewhat more readily by boiling H_2O and most readily by alkalis, evolving N as NH_3 .
N attracts Al
1. less strongly than O,
2. more strongly than P?

 O_3Al_2 . [$Al^{1/3}, O^{1/2}$] = 63,370.

Very stable body. Cannot be reduced by C at ordinary temps^o. At the temp^o of the electric furnace, however, partial reduction occurs. Seems stable at the highest temps^o. Cannot be reduced by H.
Al attracts O
1. a little less strongly than F,
2. more strongly than S.

 F_3Al . [$Al^{1/3}, F$] = 66,650.

Very stable body. Can be obtained by action of HF on Al_2O_3 . Unacted on by air or acids or aqueous alkalis. Volatile at a bright red heat.
Al attracts F
1. more strongly than O (a little),
2. more strongly than Cl

Na and Al.

Al alloys with Na, and the alloy very easily decomposes water.

Mg and Al.

Al alloys with Mg. Boudouard's researches (1901, 1902) show that the definite compounds AlMg, AlMg₂, Al₃Mg probably exist. Al, however, seems to have but a feeble affinity for Mg.

Al and Al.

According to Heycock and Neville the molecule of Al in dilute soln. in Sn is perhaps diatomic. Nevertheless Al atoms probably attract each other but feebly.

Si and Al.

Al and Si mix in nearly all proportions when fused together. But they do not seem to combine together chemically. Al and Si have in fact but a feeble affinity for each other.
Al attracts Si
1. less strongly than C,
2. more strongly than Al,
3. less strongly than P,
4. more strongly than Ge.

P and Al.

Al powder burns when heated to redness in vapour of P, forming Al_3P_4 . Al + P heated to a white heat in a current of H₂ yields Al_3P_3 . Al_3P + AlP may be obtained by use of the electric furnace.
All these phosphides are decomposed by H_2O , yielding PH_3 + $Al(OH)_3$.
Al attracts P
1. less strongly than N?
2. less strongly than S,
3. more strongly than Si,
4. more strongly than As.

 S_3Al_2 .

Can be produced by heating together Al + S. Unstable substance. Decomposed by H_2O with evolution of H_2S . Melts with difficulty. Is stable in absence of air at high temps^o.
Al attracts S
1. less strongly than O,
2. less strongly than Cl,
3. more strongly than P,
4. more strongly than Se.

 Cl_3Al . [$Al^{1/3}, Cl$] = 53,660.

Fumes in moist air, giving off HCl. Easily decomposed (to Al_2O_3 + HCl) by steam. Partly decomposed by O at a red heat, evolving Cl. Decomposed below a red heat by K or Na with production of Al. Undecomposed in N at 1500^o.
Al attracts Cl
1. less strongly than F,
2. more strongly than Br,
3. more strongly than S.

Cu and Al.

[$Al^{1/3}, Cu^{2/3}$] = 6,900.
Al combines with Cu to form alloys which are characterised by their stability. A small quantity of heat is evolved. Al has thus a perceptible affinity for Cu and a definite compound Cu_2Al exists.

Zn and Al.

Luginin and Schukareff (1902) showed that when Zn and Al alloy together, in no case is the thermal change great enough to be depended on, and no definite compound of Zn and Al is indicated. Al has in fact but a feeble affinity for Zn.

Ga and Al.

No alloy seems to have been described.

Ge and Al.

No alloy been described.

As and Al.

Al and As combine when heated together. Al will burn in vapour of As. The Al arsenide thus produced is a black solid which is decomposed quantitatively by H_2O ; AsH_3 being evolved.
Al has a considerable affinity for As, probably attracting As.
1. less strongly than P
2. more strongly than Sb
3. more strongly than Ge?
4. less strongly than Se.

Se and Al.

Finely divided Al mixed with Se and heated, combines forming Al_2Se_3 . Yellow mass, decomposed by H_2O , evolving H_2Se and forming $Al_2O_3 \cdot xH_2O$.
Al attracts Se
1. less strongly than S
2. more strongly than Te
3. more strongly than As
4. more strongly than Br.

 Br_3Al . [$Al^{1/3}, Br$] = 41,000.

Solid. Al_2Br_6 is decomposed into Al_2O_3 + HBr when heated in air. Aqueous solution on evaporation in vacuo yields crystals of $Al_2Br_6 \cdot 6H_2O$. This solution is decomposed on heating into $Al(OH)_3$ + HBr.
Al attracts Br
1. less strongly than Cl
2. more strongly than I
3. more strongly than Se.

Ag and Al.

Al alloys readily with Ag, to form alloys which are characterised by their stability and hardness. A definite compound $AlAg_2$ exists.
Al has a perceptible affinity for Ag.

Cd and Al.

According to Wright (1894) cadmium is but slightly soluble in Al; and Al practically not at all in Cd. Al seems to have but a feeble affinity for Cd; probably less for Zn than for Ag.

In and Al.

No alloy been described.

Sn and Al.

Al alloys readily with Sn and forms alloys which are characterised by their hardness and stability a definite compound AlSn has been isolated.
Al has probably a small but perceptible affinity for Al.

Sb and As.

Al and Sb combine when heated together to form a definite compound SbAs. According to Matignon (1900) Al burns in vapour of Sb. Fouzes-Diacon (1900) states that a mixture of Sb and Al is not ignited by a fuse of Mg or an Al cartridge (a mixture of Al + BaO_2 fastened to a strip of Mg). Its combustion may be effected, however, by adding a small quantity of Na_2O_2 . The product is a black friable mass, which when treated with H_2O evolves a considerable amount of SbH_3 . Al has an appreciable affinity for Sb, attracting it.
1. less than As or Te
2. more than Sn or Bi.

 Te_3Al_2 .

Al and Te when heated together combine with explosive violence to form Al_2Te_3 . Brown powder. Exposure to moist air decomposes it, TeH_2 being evolved. Thrown into H_2O it is rapidly decomposed.
Te attracts Al
1. more strongly than Sb
2. less strongly than Se
3. less strongly than I.

 I_3Al .

Al and I combine together when heated. White plates. Decomposed by heating in O.
Al attracts I
1. less strongly than Br
2. more strongly than Te

Au and Al.

Al seems to combine readily with Au to produce a series of definite compounds Al_2Au , $AlAu$, $AlAu_2$, Al_3Au_5 . Neville's experiments (1894,00) show that Au and Al form an unstable insol. compound $AuAl_2$, the gold having the power of completely withdrawing Al out of a solution in fused tin. Al therefore seems to have a consid. affinity for Au.

Hg and Al.

Al dissolves and diffuses but slowly in Hg. Al however can by heating be amalgamated with Hg. Al has but a feeble affinity for Hg.

Tl and Al.

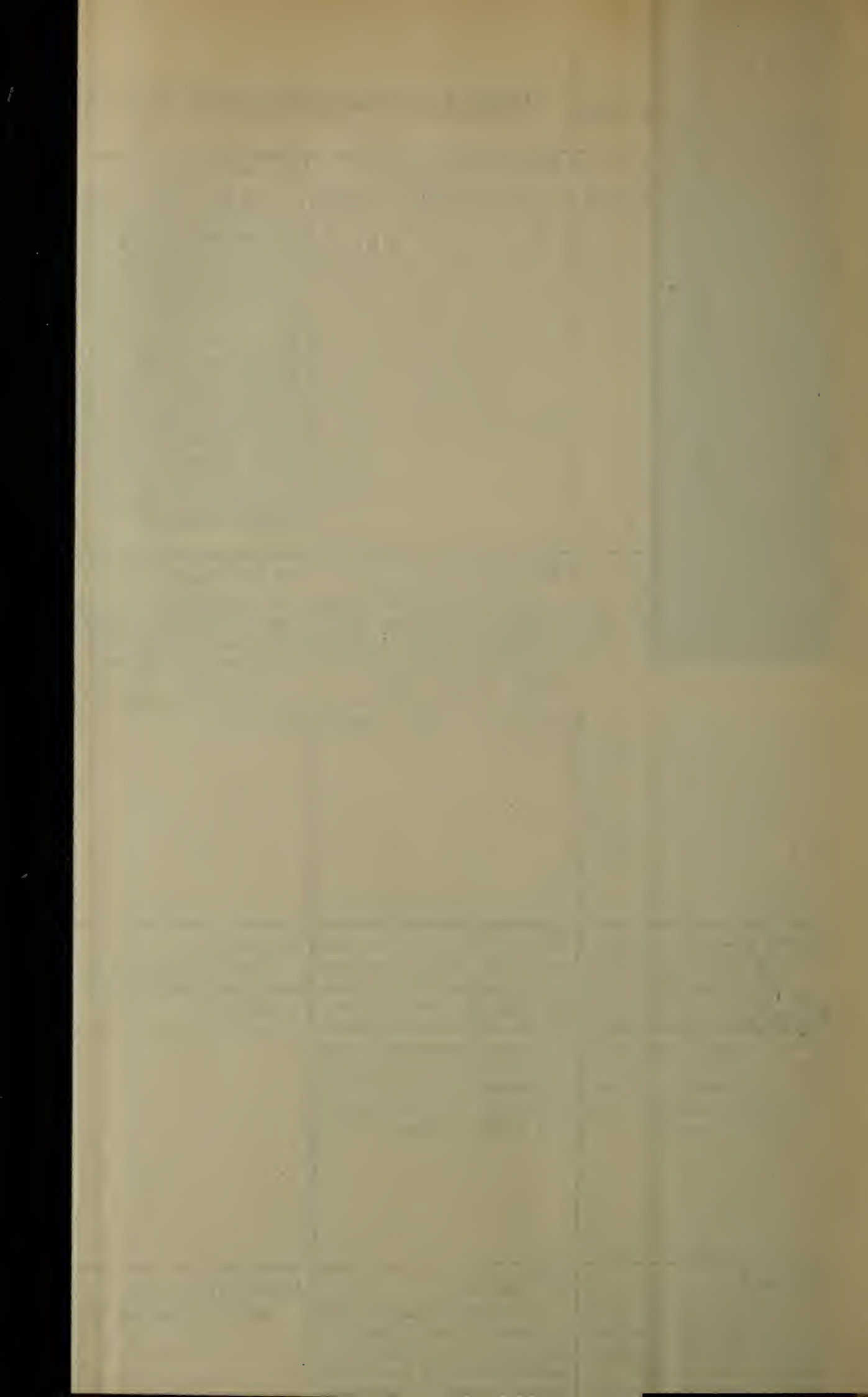
No alloy been described.

Pb and Al.

Al alloys with Pb, but no definite compounds seems to have been isolated.

Bi and Al.

Al alloys with Bi, but no definite compound seems to have been described.



H and Si.

[Si¹, H] = 8,200.

SiH₄ is decomposed completely to Si and H by heating above 400°. Takes fire in air when heated.

Data of determining the intensity of the force with which the various elements of the primary system A attract Silicon.

Li₂Si. Li and Si combine directly when heated to dull redness in a vacuum. Decomposed in a vacuum when heated above 600° into Li + Si; but is stable at 400–500°. Decomposed violently by H ₂ O. Inflames in Cl, HCl, H ₂ SO ₄ , HNO ₃ . Burns when heated in air. Heated in H to 600° yields Li ₂ H + Si. Si attracts Li 1. more strongly than H, 2. more strongly than Na, 3. less strongly than Be.	Be₂Si? Be readily combines with Si. When Be is prepared in porcelain vessels a portion of the Si is reduced and as much as 20% Si may combine with the Be to form a hard brittle mass. Be seems to attract Si 1. more strongly than Li, 2. more strongly than Mg?	B₂Si and B₆Si. Obtained by Moissan by heating Si + B in the electric furnace. Product is a mixture of these borides. SiB ₂ is readily oxidised by boiling HNO ₃ ; SiB ₃ is only slowly attacked. SiB ₃ is decomposed by fused KOH. SiB ₆ is unaffected. These Si borides are intermediate between the diamond and the ruby in scale of hardness. Both seem to be about equally stable. Decomposed by F and at higher temperatures by Cl and Br. But not by I, N, or S. Superficially oxidised by heating in air. Not effected by haloid acids. Slowly decomposed by boiling conc. H ₂ SO ₄ .	CSi. C and Si readily unite in a fused medium at 1300 to 1400°. Also formed by C + SiO ₂ in the electric furnace. Is a body of altogether extraordinary stability, not affected by O at temperatures of blow-pipe. S vapour is without action. Cl at 600 attacks slowly; action complete at 1200°. Fused KNO ₃ , KClO ₃ , boiling H ₂ SO ₄ , HNO ₃ , HCl, aqua regia do not attack it. Fused PbCrO ₄ oxidises it, but with difficulty. It is very hard, between corundum and diamond. C seems to attract Si very strongly. Si attracts C 1. more strongly than B, 2. more strongly than N.	N₂Si₂. Formed by acting on SiCl ₄ with NH ₃ , or by heating very strongly Si in N. Infusible white powder, which is not dissolved by any acid except HF. Aq which produces NH ₄ SiF ₆ . Slowly decomposes in moist air producing NH ₃ . Melted with KHO gives NH ₃ + K silicate. Si ₃ N ₂ like BN is a very stable body.	O₂Si. [Si ¹ , O ¹] ₂ = 54,800. It stable at the highest temperature and cannot be reduced by H or C. It is reduced by Mg. Very stable body O attracts Si 1. much more strongly than S, 2. more strongly than F? SiO ₂ seems very much more stable than SiF ₄ .	F₂Si. [Si ¹ , F] = 67,300(?) Formed by passing BF ₃ vapour through a red hot tube of porcelain. Also by action of HF + SiO ₂ . Gas. Decomposed by electric sparks with separation of Si. K and Fe when hot burn in SiF ₄ forming fluorides and Si. Moist air forms an oxy-fluoride. Water decomposes SiF ₄ forming SiO ₂ ·xH ₂ O and H ₂ SiF ₆ . SiF ₄ does not seem a stable body and I am inclined to believe the above thermal data is much too high. Si attracts F 1. less strongly than O? SiO ₂ seems much more stable than SiF ₄ . 2. more strongly than Cl.
Na₂Si? Na and Si do not combine directly together when heated. No silicide has been isolated. Si attracts Na 1. less strongly than Li, 2. less strongly than Cu? 3. less strongly than Mg.	Mg₂Si. Mg combines readily with Si when heated with it in the electric furnace. Also readily produced by heating SiO ₂ + Mg. Acted on by strong HCl evolving SiH ₄ . Water attacks it in the cold with the evolution of H. Since Mg and Si when heated together in a glass tube to a dull red heat combine with glowing, it is certain that Mg has a considerable affinity for Si. Si attracts Mg 1. less strongly than Be? 2. more strongly than Na, 3. more strongly than Zn, 4. more strongly than Al.	Al and Si. Al and Si mix in nearly all proportions when fused together. But they do not seem to combine chemically. Al and Si have in fact but a feeble affinity for each other. Si attracts Al 1. less strongly than B, 2. less strongly than Mg, 3. less strongly than Si.	Si and Si. Si atoms attract each other with a considerable force. This is indicated by many facts; e.g. Si is very infusible and involatile, it forms an enormous number of complex silicates in which Si atoms are undoubtedly directly united together. Yet Si atoms do not cohere together so strongly as C atoms. For example HOOSi.SiO.SiOOH with only 3 Si atoms arranged in series is converted by soda with evolution of H into silica, in which self combination of Si cannot be assumed.	P and Si. No silicide of P been prepared.	S₂Si. [Si ¹ , S] ₂ = 5,000. Formed by heating Si + S. Unchanged in dry air at ordinary temperatures. Decomposed by moist air to H ₂ S and SiO ₂ . Decomposed rapidly by water and alcohol. Burns to SiO ₂ + when heated in air.	Cl₂Si. [Si ¹ , Cl] = 39,400. Si ₂ Cl ₆ and SiCl ₄ are also known. SiCl ₄ is a mobile liquid. Formed by Cl + SiO ₂ + C at a red heat. The presence of C is not necessary if the temperature is high enough. Heated to redness with H, SiHCl ₃ is formed. SiCl ₄ is decomposed by passing the vapour with dry air through a white hot tube. H ₂ S forms SiCl ₃ SH when SiCl ₄ and H ₂ S are passed through a red hot tube. Many metals eg. K, Na, Zn, Ag with draw all the Cl from SiCl ₄ when heated to redness in vapour of SiCl ₄ . Si attracts Cl 1. more strongly than S, 2. less strongly than F, 3. more strongly than Br.
Cu₂Si. Formed by heating Cu + Si in the electric furnace, until the excess of Cu volatilises. Decomposed energetically by acids, Cl, Br, I, F; reduced by H ₂ O vapour. Heated with S the Si is partially liberated (showing that Cu attracts S a little more strongly than Si). Cu has therefore only a feeble affinity for Si. Si attracts Cu 1. more strongly than Na, 2. more strongly than Ag, 3. more strongly than Zn.	Zn and Si. Zn does not combine directly with Si, simply dissolving in it. Zn has, therefore, only a feeble affinity for Si. Si attracts Zn 1. less strongly than Mg, 2. more strongly than Cd, 3. less strongly than Cu.	Ga and Si. No silicides known.	Ge and Si. No nitride known.	As and Si. No silicide known.	Se and Si. No compound been prepared.	Br₂Si. Prepared by direct union of hot Si + Br.vap., also by heating Br + SiO ₂ + C. liquid; decomposed to SiO ₂ by water. Shaken with conc. H ₂ SO ₄ , slowly decomposes to Br + SiO ₂ . Si attracts Br 1. more strongly than I, 2. less strongly than Cl, 3. more strongly than Se.
Ag₂Si. Ag and Si do not directly unite. Ag when heated with Si in the electric furnace dissolves a considerable quantity of Si, but the Si separates as the metal cools and no Ag silicide is obtained nor does the Si retain any silicon. Ag has therefore only a very feeble affinity for Si. Ag attracts Si 1. more feebly than Cu, 2. more strongly than Au?	Cd and Si. Cd does not combine with Si at all. Si simply dissolves in the Si.	In and Si. No silicides known.	Sn and Si. Sn and Si do not unite when heated together. But Si dissolves in Sn. Sn has but a feeble affinity for Si.	Sb and Si. Sb does not combine with Si directly, but dissolves the Si. Sb has therefore only a very weak affinity for Si.	Te₂Si. No silicide of Te known.	I₂Si. [Si ¹ , I] = 14,500. Formed by heating Si + I strongly in CO ₂ . Also by heating Mg + SiO ₂ + CO ₂ + I. Colourless crystals. Vapour burns when heated in air with separation of Si. Water produces SiO ₂ + H ₂ O + HI. Si ₂ I ₆ melts at 256° in a vacuum with partial decomposition. When heated decomposes to SiI ₄ + SiI ₂ . With H ₂ O gives H ₂ Si ₂ O ₄ + HI. I attracts Si 1. less strongly than Br, 2. more strongly than Te?
Au and Si. Au and Si do not directly unite and no compound of Au and Si has been obtained. Au has like Ag only a very feeble affinity for Si.	Hg and Si. Warren (1893) finds that Hg and Si cannot be made to combine. Si, in fact, has but a very feeble affinity for Hg.	Tl and Si. No silicides known.	Pb and Si. Pb and Si do not unite when heated together. They simply dissolve. Pb has but a feeble affinity for Si.	Bi and Si. Same as antimony.		

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B, Al, Ga, In, Tl. The affinity is small but perceptible at B, and sinks as we pass towards Tl.

B 3.5; Al 2.0; Ga 2.5; In 1.5; Tl 0.4.

C, Si, Ge, Sn, Pb. C has a considerable affinity for Al; the affinity slowly decreases as we pass from C to Pb.

C 5; Si 3; Ge 2.5; Sn 2; Pb 0.5.

N, P, As, Sb, Bi. The affinity at Al is considerable at N and steadily decreases as we pass from N to Bi.

N 10; P 5; As 4.5; Sb 3.5; Bi 3.

O, S, Se, Te. O has a very great affinity for Al and the affinity steadily decreases as we pass towards Te.

O 15.8; S 8; Se 6.5; Te 6.

F, Cl, Br, I. All have a very great affinity for Al, the affinity falling from F to I.

F 16.7; Cl 13.4; Br 10.25; I 8.

Silicon

Longitudinal Sections.

H, Li, Na, Cu, Ag, Au. The attraction for Si is feeble for all these elements, it rises from H to Li, then falls from Li to Au.

H 2.0; Li 4.0; Na 25; Cu 2.0; Ag 1.0; Au 0.5.

Be, Mg, Zn, Cd, Hg. The attraction for Si seems to decrease as we pass from B towards Hg.

Be 6; Mg 6; Zn 1.0; Cd 0.5; Hg 0.5.

B, Al, Ga, In, Tl. The attraction for Si seems to fall steadily from B to Al and probably to Tl.

B 8.0; Al 7.0; Ga 1.0; In 1.0; Tl 0.5.

C, Si, Ge, Sn, Pb. The affinity for Si is great at C, and falls rapidly as we pass towards Pb, becoming very small at the latter point.

C 14; Si 15; Ge 1.0; Sn 0.5; Pb 0.5.

N, P, As, Sb, Bi. The attraction for Si is considerable for N, and is very small for Sb and Bi. Hence the following sections.

N 15; P 4.0; As 1.0; Sb 0.5; Bi 0.5.

O, S, Se, Te. The attraction for Si seems to fall steadily from O to T.

O 13.7; S 1.25; Se 1.2 ?; Te 1.2 ?;

F, Cl, Br, I. The attraction for Si is greatest for F and smallest for I.

F 13; Cl 10; Br 8; I 3.5.

Cross Sections.

Li, Be, B, C, N, O, F. The attraction for S rises from Li to N, attains a maximum at N and slowly decreases as we pass towards F.

Li 4; Be 6; B 8; C 14; N 15; O 13.7; F 13.

Na, Mg, Al, Si, P, S, Cl. The affinity rises from Li to Mg, attains a maximum at Si, sinks again, attaining a minimum at S, and again rises at Cl.

Na 2.5; Mg 6.0; Al 7.0; Si 15; P 4; S 1.25; Cl 10.

Phosphorus.

Cross Sections.

Li, Be, B, C, N, O, F. Li seems to have an appreciable affinity for P, and the affinity seems to sink as we pass from Li to C, attaining here a minimum value. It then rises attaining a maximum at N.

Li 5; Be 4; B 3; C 1; N 12; O 9.25; F 8.

Na, Mg, Al, Si, P, S, Cl. Na seems to have a considerable affinity for P, and the affinity probably sinks until Si is reached; it then seems to rise, attaining a maximum value at P; sinking somewhat for S, and rising again for Cl.

Na 5; Mg 4; Al 3; Si 1; P 7; S 4; Cl 6.25.

Cu, Zn, Ga, Ge, As, Se, Br. Cu and Zn have a considerable affinity for P; As has but a feeble affinity for P, the affinity steadily increasing as we pass from As to Br, and attains a maximum at Br.

Cu 3; Ga 3; Zn 3; Ge 2; As 1; Se 3.5; Br 4.15

Ag, Cd, In, Sb, Te, I. Ag has but a feeble affinity at P, the affinity seeming to rise as we pass from Ag to Cd, attaining a maximum at Sn, then sinking as we pass from Sn to Sb, and then rises steadily, attaining its greatest value at I.

A 0.5; Cd 2; In 2; Sn 2; Sb 0.5; Te 2; I 2.5.

H₃P. [P^{1/2}, H] = 3,860.

Very unstable. Decomposed by light. Easily decomposed by heat by passing through a red hot tube. Burns in air at 150°. Decomposed by electric sparks.

Data for determining the intensity of the force with which the various elements of the primary system A attract Phosphorus.

<p>Li and P.</p> <p>According to Troost, Li and P combine together when heated to form a brown substance which is decomposed by water with evolution of PH₃.</p>	<p>Be and P.</p> <p>Described by Wöhler as a greyish powder obtained by heating Be in P vapour.</p>	<p>B and P.</p> <p>Besson describes a boride formed by heating B.Br₃.PH₃ to 300°. Brown powder. Insol. in H₂O. Reacts with boiling conc. alkalis to give PH₃. Gives off P when heated to redness in N or H.</p> <p>Moissan describes a boride PB which is not volatile in vacuo at 500°. At 200° in O burns. Throwing into fixed alkali nitrates there is incandescence. Boiling H₂O has no action on the phosphide, but H₂O vapour decomposes it. Heated in vacuo to a high temperature it loses P and goes into B₂P₃. PB is converted by Cl into BCl₃ + PCl₅ with incandescence.</p> <p>B₂P₃ is more stable than PB, does not burn in Cl below a red heat. Does not inflame in HNO₃. P has therefore a considerable affinity for B.</p> <p>P attracts B</p> <ol style="list-style-type: none"> 1. more strongly than C. 2. more strongly than Be. 	<p>C and P.</p> <p>No carbide of P has been described. Probably exists.</p>	<p>N and P.</p> <p>P₃N₅. A very stable body, only acted on by Cl at temperatures above that at which hard glass melts. And only at a little higher temperature does O act on it. Only in traces decomposed by boiling water. But heated in a sealed tube in H₂O to 180° gives H₃PO₄ + NH₃. Not acted on by HNO₃. Decomposes at a bright red heat when heated in N or H or in a vacuum into its elements.</p> <p>P attracts N</p> <ol style="list-style-type: none"> 1. more strongly than C. 2. more strongly than O? <p>(for O does not act on P₃N₅ below the B.Pt. of hard glass).</p> <ol style="list-style-type: none"> 3. more strongly than P? 	<p>O and P.</p> <p>[P^{1/2}, O^{1/2}] = 37,000.</p> <p>P₂O₅ seems to be stable at a white heat. Can be reduced by heating with Fe, K, Na, &c. Probably also with C (since P is produced by reducing phosphates with C).</p> <p>P attracts O</p> <ol style="list-style-type: none"> 1. less strongly than N? 2. more strongly than F. 3. more strongly than S. 	<p>F and P.</p> <p>PF₃. Gas. Not acted on by O₂; is incombustible; not acted upon by S vapour at 440°. Hence P attracts F more strongly than S does. Decomposed by powerful electric sparks, but not by ordinary sparks. PF₃ is less stable than PF₅. Decomposed by heat. Decomposed by hot Si to form SiF₄. In a glass apparatus P + SiF₄ is formed. Very slowly decomposed by H₂O, forming H₃PO₃ + HF. More rapidly decomposed by steam at 100°.</p> <p>P attracts F</p> <ol style="list-style-type: none"> 1. less strongly than O? 2. more strongly than Cl.
<p>Na and P.</p> <p>Na and P combine with the evolution of much heat by merely adding P to Na under rock oil. Na₃P, a black solid, may be kept in dry air. In moist air, water, or acids, it gives off inflammable PH₃. Na seems to have a considerable affinity for P.</p> <p>Na seems to attract P</p> <ol style="list-style-type: none"> 1. more strongly than Mg. 2. more strongly than Cu? 	<p>Mg and P.</p> <p>Mg₃P₂ is formed by heating P vapour + Mg in a current of H. Also by melting P + Mg in sealed tube. Readily decomposed by H₂O. Dry air or O is without action at ordinary temperatures, but burns in O at a red heat. Also burns brilliantly when heated in Cl, I, Br. HCl decomposes it with liberation of PH₃. Acids form Mg salts + PH₃.</p> <p>Mg attracts P</p> <ol style="list-style-type: none"> 1. less strongly than Na. 2. more strongly than Al. 	<p>Al and P.</p> <p>Al powder burns when heated to redness in vapour of P, forming Al₃P₃.</p> <p>Al + P heated to a white heat in a current of H yields Al₃P₃. Al₃P and AlP may be obtained by the use of the electric furnace. AlP may be produced by igniting red P + Al. All these phosphides are decomposed by H₂O, yielding PH₃ + Al(OH)₃.</p> <p>P attracts Al</p> <ol style="list-style-type: none"> 1. less strongly than Mg. 2. more strongly than Si. 	<p>Si and P.</p> <p>No compound of P and Si has been isolated. Probably but a feeble affinity exists between Si and P.</p>	<p>P and P.</p> <p>At temperatures between 500° and 1000° the molecule is P₄. At 1500—1700° the molecule is P₂. The mol. wt. of P in C₆H₁₁ lies between P₂ and P₄. P atoms have a considerably affinity for each other.</p>	<p>S and P.</p> <p>[P₄, S₈] = 36,800.</p> <p>P and S combine when heated together, often with violent explosion, to produce several compounds such as P₄S₃, P₂S₅, PS₂, P₂S₇. Most seem to be decomposed by H₂O with production of acids of P and H₂S.</p> <p>P attracts S</p> <ol style="list-style-type: none"> 1. less strongly than O. 2. less strongly than Cl. 3. more strongly than P. 	<p>Cl and P.</p> <p>[P^{1/2}, Cl] = 25,100; [P^{1/2}, Cl] = 21,000;</p> <p>P and Cl combine to produce PCl₃ and PCl₅. PCl₃ seems the most stable. PCl₃ is decomposed by moist air; or by H₂O; to HCl + H₃PO₄.</p> <p>P attracts Cl</p> <ol style="list-style-type: none"> 1. less strongly than F. 2. more strongly than S. 3. more strongly than Br.
<p>Cu and P.</p> <p>Cu and P readily combine when heated together to form various compounds such as Cu₃P, Cu₂P, Cu₃P₂, Cu₄P₃. Cu and P may be melted together in all proportions. The substances seem very analogous to alloys. Most are stable in the air, unacted on by HCl, usually oxidised by HNO₃. Cu₃P heated out of contact with air yields CuP + P. Is readily attacked by Cl or Br. Phosphides of Cu can be produced by heating CuCl with P vapour.</p> <p>P attracts Cu</p> <ol style="list-style-type: none"> 1. less strongly than Na. 2. most strongly than Ag. 3. more strongly than Zn. 	<p>Zn and P.</p> <p>Zn and P combine together, producing phosphides. Zn₃P₂ seems to exist. Also formed by strongly heating a mixture of NaPO₃ and Zn shavings in a retort. Zn phosphides are not decomposed by water but are slowly decomposed by HCl giving PH₃.</p>	<p>Ga and P.</p> <p>No phosphide investigated.</p>	<p>Ge and P.</p> <p>No phosphide known.</p>	<p>As and P.</p> <p>P does not combine directly with As. By passing PH₃ into PCl₃ get a precipitate of PAs. Heated in absence of air, or CO₂, P sublimates and then As. Decomposed by H₂O. Burns when heated in air. Also by KOH.Aq to decompose PAs producing PH₃. P seems to have but a feeble affinity for As, but a stronger affinity than Sb has.</p>	<p>Se and P.</p> <p>P and Se unite directly together to form 4 phosphides P₄Se, P₂Se, P₂Se₃, P₂Se₅. P₄Se takes fire in air, is a liquid, decomposed by water containing air. All seem more or less easily decomposable by water. Burns when heated in air. Se seems to have but a feeble affinity for P.</p> <p>P attracts Se</p> <ol style="list-style-type: none"> 1. more strongly than As. 2. less strongly than Br. 3. less strongly than S. 4. more strongly than Te. 	<p>Br and P.</p> <p>[P^{1/2}, Br] = 16,600.</p> <p>P and Br combine violently together to form PBr₃ and PBr₅. PBr₃ is decomposed slowly by cold H₂O. PBr₅ decomposes to PBr₃ + Br₂ at 100°.</p> <p>P attracts Br</p> <ol style="list-style-type: none"> 1. more strongly than I. 2. less strongly than Cl. 3. more strongly than Se.
<p>Ag and P.</p> <p>Ag has but a little affinity for P. Granger states that when P vapour is passed over Ag heated to 400°, combination takes place and Ag₃P is formed. Ag has the peculiarity of combining with P at 400°, giving it up at 500°, combining with it again at 900°. Ag₂P when heated in a current of inactive gas at the temperature of its formation is completely decomposed. Ag has but a feeble affinity for P.</p> <p>P attracts Ag</p> <ol style="list-style-type: none"> 1. less strongly than Cu. 2. more strongly than Au. 3. less strongly than Cd. 	<p>Cd and P.</p> <p>Cd and P combine when heated together to form a grey phosphide, which burns in air to phosphide and is decomposed by HCl with evolution of PH₃.</p> <p>According to Renault when P vapour is passed over hot Cd, two phosphides Cd₃P₂ and Cd₂P are formed.</p>	<p>In and P.</p> <p>No phosphide investigated.</p>	<p>Sn and P.</p> <p>Sn and P combine together when heated. Two definite compounds SnP and SnP₂ seem to exist. According to Emmerling they are not attacked by HCl.</p> <p>P attracts Sn</p> <ol style="list-style-type: none"> 1. more strongly than Sb. 2. more strongly than Pb. 	<p>Sb and P.</p> <p>Granger (1898) states that P and Sb do not combine directly. According to Macivor by the action of P (in CS₂) or SbBr₃ (in CS₂) a red powder P.Sb is obtained.</p> <p>Sb appears to have but a feeble affinity for P.</p>	<p>Te and P.</p> <p>Oppenheim obtained a black amorphous solid giving off fumes of P₂O₅ in air, by heating P with powdered Te. P has but a feeble affinity for Te.</p>	<p>I and P. [P^{1/2}, I] = 3,630.</p> <p>P and I combine directly, with production of much heat to form PI₃ and PI₅. Both decomposed by heating in O to P₂O₅ and I. Decomposed by H₂O.</p> <p>P attracts I</p> <ol style="list-style-type: none"> 1. less strongly than Br. 2. more strongly than Br. 2. more strongly than Te.
<p>Au and P.</p> <p>Granger (1896—1898) states that P can be distilled away from finely-divided Au without affecting it. But at about 400° its vapour attacks the metal, which swells up to form Au₃P₂. At a dull red heat again, Au is not attracted by P, so that combination only occurs between comparatively narrow temperature ranges. Au₃P₂ is decomposed when heated in air and also slowly but completely when heated to about 400° in a current of inactive gas. AuCl₃ heated with P is decomposed to metallic Au. Au has but a feeble affinity for P.</p> <p>P attracts Au</p> <ol style="list-style-type: none"> 1. less strongly than Ag. 	<p>Hg and P.</p> <p>According to Emmerling, Hg when heated with P in a sealed glass tube, is not attacked. Granger shows that when P₂I₄ is heated with Hg, the phosphide Hg₃P₄ is obtained in hexagonal prisms. It is easily decomposed by heat. Hg seems to possess but a very feeble affinity for P.</p> <p>Hg attracts P</p> <p>less strongly than Cd</p>	<p>Tl and P.</p> <p>No compound of Tl and P has been isolated with certainty. According to Crookes, the black substance formed by passing P hydride into amm. Tl₂SO₄ is a phosphide of Tl. Carstanien failed to obtain a phosphide by heating the elements together, or by reducing Tl₂PO₄ by C or H. Flemming found that a thin black coating is formed on molten Tl when pieces of P are thrown on it.</p> <p>Tl certainly possesses but a feeble affinity for P.</p>	<p>Pb and P.</p> <p>Pb does not unite directly with P and no phosphide of Pb has been isolated. According to H. Rose, a brown precipitate consisting of a phosphide of Pb, is obtained by passing PH₃ into PbAc solution.</p> <p>Pb has certainly only a very feeble affinity for P.</p>	<p>Bi and P.</p> <p>Bi and P do not combine directly. According to Berzelius a phosphide is formed by leading PH₃ into Bi(NO₃)₃ solution. Bi has certainly but a feeble affinity for P.</p>		



H₂S. [S^{1/2}, H] = 2,300.
Is easily decomposed. When heated to ca. 400° is decomposed to H and Se. Also decomposed by electric sparks.

Data for determining the intensity of the force with which the various elements of the primary system A attract Sulphur.

Li₂S. [Li², S, Aq] = 58,000.
Li and S combine when heated together. Li₂S is obtained by reducing Li₂SO₃ by C. Sol. in H₂O and alcohol.
S attracts Li
1. more strongly than H,
2. more strongly than Na?
3. more strongly than Be.

BeS.
Described by Wöhler as a greyish fused mass, which evolves H₂S by the action of acids. Obtained by heating Be in S vapour. No sulphide is produced by heating BeO in S or CS₂ vapour. According to Nilson and Pettersson, Be and S do not combine when heated together.
Be attracts S
1. less strongly than Li,
2. more strongly than B?
3. less strongly than Mg?

B₂S₃. [S^{1/2}, B^{1/3}] = 13,800.
B₂S₃ is a white solid, easily volatile. Unstable. Decomposed H₂S + H₂BO₃ by moist air or by H₂O — with violence in the last case. May be obtained by action of H₂S on B at a bright red heat. Burns in Cl at ordinary temperatures; in O at a red heat.
B₂S₃ dissociates at 390° in a vacuum to B₂S₃ + S. It is less stable than B₂S₃.
S attracts B
1. less strongly than Be?
2. more strongly than C,
3. less strongly than Al?

CS₂. [C¹, S^{1/2}] = -6,500.
C and S combine directly when heated, to form a volatile liquid, CS₂. Not stable. Easily inflammable. Heated strongly give C and S. Decomposed by many metals.
A compound CS is also known. At 200° gives C and S.
S attracts C
1. less strongly than B,
2. more strongly than N,
3. less strongly than C.

NS. [S^{1/2}, N^{1/2}] = -16,000.
Unstable body. Decomposes at 160° with slight explosion. Explodes violently when rubbed or struck with a hammer. Slowly decomposed by H₂O, also by KOH, HCl, &c.
S attracts N
1. less strongly than C,
2. less strongly than O,
3. less strongly than P.

O and S. [S^{1/2}, O] = 36,000.
S inflames in O when heated. Produces several oxides, viz SO₂, SO₃, &c. SO₂ is not decomposed by passing through a red hot tube, but by heating to about 1200° it changes to S + SO₃. Is reduced by red hot C. K and Sb burn in SO₂. SO₃ parts with O at a red heat.
S attracts O
1. much more strongly than N,
2. less strongly than F.

F and S.
S when brought into contact with F, burns vividly, producing SF₆ and lower fluorides. SF₆ is a very stable gas. Incombustible. P, B, Si, Ag, Cu when heated with it to a red heat do not decompose. Na and Se, however, decompose it. KOH whether fused or in alcoholic solution does not decompose it. No change when heated up to the melting point of hard glass. At the temperature of the electric spark, however, it is partially decomposed. It is decomposed when heated with Na or Se. Sparked with H and O it is decomposed.
S attracts F
1. more strongly than O?
2. more strongly than Cl.

Na and S.
Na and S combine when heated together with the evolution of heat and light. Several compounds are known. Eg. Na₂S, Na₂S₂, Na₂S₃ &c. Na₂S solution is decomposed by acids, even by CO₂, with the evolution of H₂S. O also decomposes Na₂S solution.
S attracts Na
1. less strongly than Li?
2. more strongly than Mg,
3. more strongly than Cu?

MgS. [Mg, S] = 19,900.
Can be formed by heating Mg and S together, alkaline sulphides do not precipitate MgS from solutions of Mg salts, but Mg(OH)₂. MgS is decomposed by H₂O to Mg(OH)₂ and Mg(SH)₂. MgS is not stable.
S attracts Mg
1. more strongly than Be,
2. less strongly than Zn,
3. less strongly than Na,
4. more strongly than Al.

Al₂S₃.
Can be produced by heating together Al and S. Unstable substance. Decomposed by H₂O with evolution of H₂S. Melts with difficulty. Is stable in absence of air at high temperatures.
S attracts Al
1. more strongly than B?
2. less strongly than Mg?
3. less strongly than Ga or In,
4. more strongly than Si.

SiS₂. [Si^{1/2}, S^{1/2}] = 5.
Formed by heating Si and S, or by heating Si in H₂S. Unchanged in dry air at ordinary temperatures.
Decomposed by moist air to H₂S + SiO₂. Decomposed rapidly by water and alcohol. Burns to SiO₂ + SO₂, when heated in air.
S attracts Si
1. more strongly than C,
2. less strongly than Al,
3. less strongly than P?
4. less strongly than Se.

P and S. [P¹, S₂] = 36,000.
P and S combine when heated together, often with violent explosion and production of much heat and light, to produce several compounds such as P₄S₃, P₂S₅, P₂S₇, P₂S₈.
Most seen to be decomposed by water, with production of acids of P and H₂S.
S attracts P
1. more strongly than Si?
2. more strongly than N,
3. less strongly than As.

S and S.
S at ordinary temperatures forms complex molecules S₂. At about 860° S₂ exists. And at very high temperatures Nerust has shown it exists as S. The fact that S can exist in several allotropic modifications shows that S atoms have a considerable affinity for each other.

Cl and S. [S^{1/2}, Cl^{1/2}] = 7,500; [S^{1/2}, Cl] = 6,000.
SCl₂ is a very unstable body; easily decomposed to S₂Cl₂ + Cl. At 86° 50' of SCl₂ is thus decomposed. S₂Cl₂ is also unstable. Cl has but a feeble affinity for Cl.
S attracts Cl
1. less strongly than F,
2. more strongly than Br.

Cu and S.
Cu has a strong affinity for S, burning with the evolution of heat and light when heated together. Cu₂S is prepared by 2Cu + S heated together. At 650° in H is reduced to Cu. Heated in CO₂ to 250—300° Cu is formed. In electric furnace fuses and goes to Cu.
CuS when heated to 330° goes into Cu₂S.
S attracts Cu
1. less strongly than Na?
2. more strongly than Ag?
3. more strongly than Zn.

Zn and S. [Zn, S, xH₂O] = 20,800.
Not formed by heating together Zn and S, as S volatilises before the temperature of combination is reached. Occurs native as Zn blend. Can be produced by heating ZnO + S. ZnS is decomposed by acids, giving H₂S. In absence of air can be heated to a high temperature. Can be heated to whiteness without decomposition.
Zn attracts S
1. less strongly than Cu?
2. less strongly than Mg?
3. more strongly than Cd?

Ga and S.
Watt's Dict. says: "The white precipitate obtained by passing H₂S into a conc. solution of GaCl₃ in NH₃ aq, to which Am. Tartrate has been added is probably a sulphide of Ga."
S attracts Ga
1. more strongly than Si,
2. more strongly than As,
3. more strongly than Sn.

Ge and S. GeS₂.
Obtained by AmHS + GeO₂ + H₂SO₄ + H₂S and drying in vacuo. White powder. Heated in dry CO₂ is partially decomposed and volatilised. GeS₂ when suspended in water decomposes after some time evolving H₂S.
GeS. Vap. Den. at 1100—1500° corresponds to GeS. Obtained by heating GeS₂ in a current of H. Heated in air gives GeO₂.
S attracts Ge
1. more strongly than Si,
2. more strongly than As,
3. more strongly than Sn.

As and S.
AsS, As₂S₃, As₂S₅ are known. Formed by heating As + S together. As₂S₃ and As₂S₅ occur native. As₂S₃ burns in air. Oxidised by HNO₃ or Cl. Heated in H get As + H₂S.
As₂S₃. Dil. acids do not act on As₂S₃. Conc. acids decompose it; also Cl, hot Fe, Ag &c. Heated with alkaline carbonates and charcoal all the As is obtained as a mirror.
As₂S₅. Heated in a stream of H is reduced to metallic As + H₂S.
S attracts As
1. more strongly than Se,
2. more strongly than Sb?
3. less strongly than Ge.

Se and S.
Se and S can be melted together in all proportions, but is very doubtful whether any definite compound is obtained. Recent work seems to prove that it is not. Se has but a feeble affinity for S.

Br and S.
It is doubtful whether any definite compound of S and Br has been isolated. Powdered S dissolves in liquid Br with the evolution of a little heat. But it is doubtful whether a compound is formed. If so it is extremely unstable at ordinary temperatures. Br in fact seems to have but a feeble affinity for S.
S attracts Br
1. less strongly than Cl,
2. less strongly than I.

Ag and S. [Ag², S] = 2,670.
Ag₂S. Prepared by directly heating Ag + S together. Heated in air slowly goes to Ag, forming SO₂. Heated in Cl, AgCl and S₂Cl₂ is formed. Reduced to Ag by action of metals and dilute acids.
Ag attracts S
1. less strongly than Cu,
2. more strongly than Au,
3. less strongly than Cd.

Cd and S.
CdS occurs native. Obtained by CdSO₄ + H₂S heated to a red heat. Also H₂S + Cd salt in solution. CdS is produced in small quantities by passing S vapour over strongly heated CdO or Cd.
Cd attracts S
1. less strongly than Zn?
2. more strongly than Hg,
3. more strongly than Ag,
4. less strongly than In.

In₂S₃.
Obtained by H₂S + In salt in solution. Also by heating In + S, or In₂O₃ + S. Solid. Infusible. With acids it gives In salts + H₂S. Heated in air it burns to In₂O₃.
In attracts S
1. more strongly than Cd?
2. more strongly than Sn?
3. less strongly than Ga?
4. more strongly than Ti?

Sn and S.
Sn and S heated together combine with evolution of heat. SnS₂ thus formed is partially decomposed by the heat to SnS + S.
SnS. Prepared by heating Sn + S. Can be sublimed at a red heat in H, but continued heating in H is said to reduce it to Sn, H₂S being given off.
Heated in air, SnS is gradually converted into SnO₂ + SO₂. Reacts with Cl at ordinary temperatures to produce SnCl₄.
SnS₂ is decomposed by heating to SnS + S. Heated in air oxidises to SnO₂ + SO₂.
Sn attracts S
1. less strongly than Ge?
2. more strongly than Pb,
3. more strongly than Sb,
4. less strongly than In?

Sb and S.
Sb₂S₃ can be prepared by heating together Sb + S. Boiling H₂O partially decomposes it to Sb₂O₃ + H₂S.
Heated in H, Sb is produced. Calcined in air, Sb₂O₃ + SO₂ is formed. Decomposed by Cl, HCl, HNO₃, Zn, Fe, KCN &c.
Sb₂S₃. Heated in absence of O gives Sb₂S₃ + S.
S attracts Sb
1. less strongly than As?
2. more strongly than Te,
3. more strongly than Bi,
4. less strongly than Sn.

Te and S.
Berzelius described two sulphides TeS₂ and TeS₃ corresponding with the oxides TeO₂ and TeO₃. According to Becker, CS₂ removes all the S from these compounds and hence concludes they are only mixtures of Te and S.
Compounds of Te and S are probably formed by passing H₂S into TeO₂ aq and TeO₃ aq. Te has but a feeble affinity for S; but a greater affinity than Se has.

I and S. [S, I] = 5,400.
S and I probably combine together when heated, but no definite compound has been isolated.
SI has been obtained by digesting together SbI + S₂Cl₂.
SI₄ is said to be obtained by evaporating together I + S + CS₂.
I has but a feeble affinity for S, but probably a greater affinity than either Te or Br have.
S attracts I
1. more strongly than Br,
2. more strongly than Te?

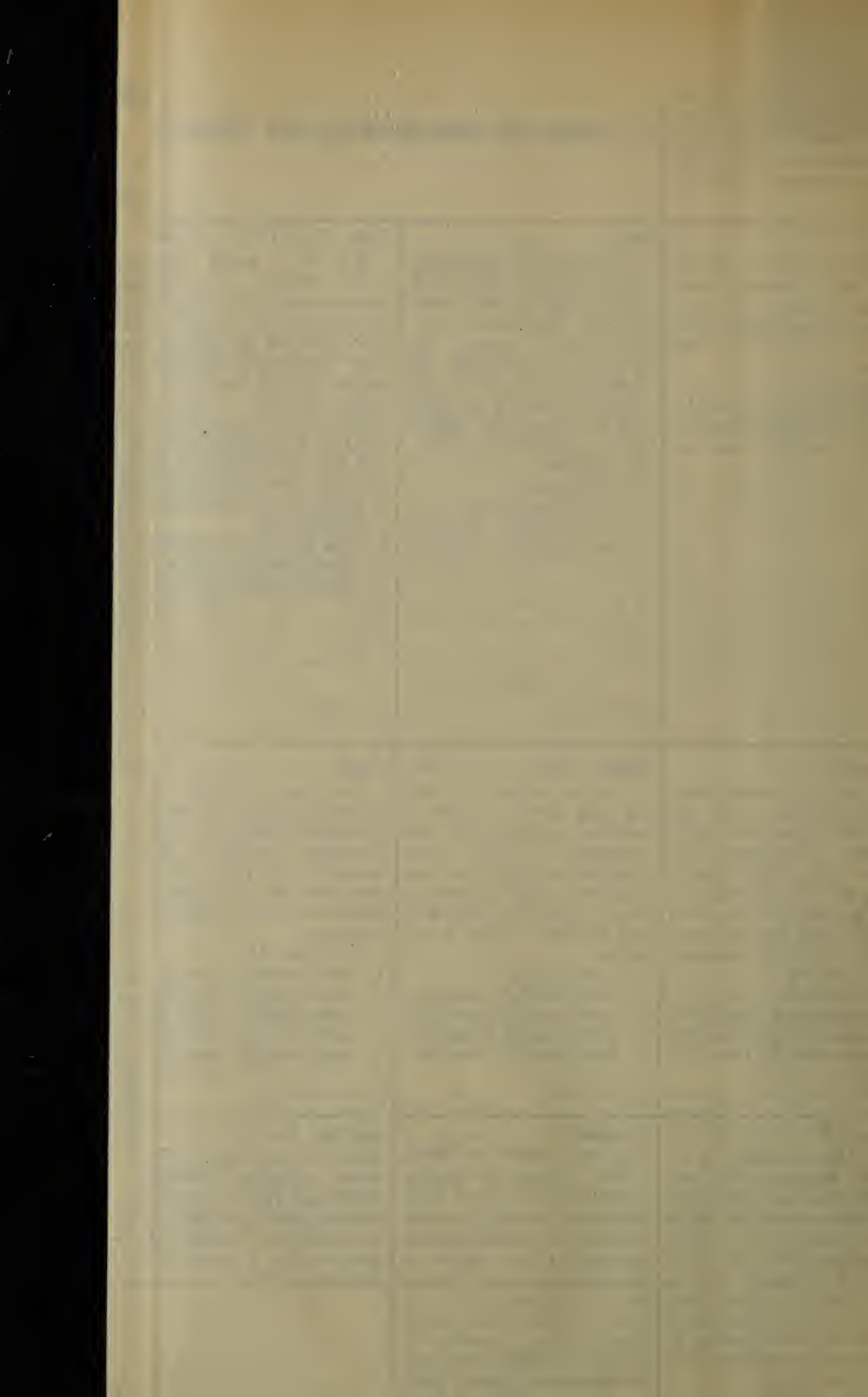
Au and S.
Au has but a feeble affinity for S. If H₂S is passed into AuCl₃ solution heated to 100°, Au is precipitated. Au₂S is completely decomposed at 240°. AuS heated to 140° in air, evolves SO₂.
At 250—270° all the S is removed without the intermediate production of Au₂S.
Au attracts S
1. less strongly than Ag,
2. less strongly than Hg.

Hg and S. [S^{1/2}, Hg^{1/2}] = 4,100.
Hg₂S and HgS are both known.
HgS is formed by rubbing or heating together S + Hg. Also by subliming HgO + S. Hg + S combine together when heated with the production of heat and light and partial projection of the mass. Heated in air Hg sublimes and SO₂ is formed. Partially decomposed to Hg + S at 670°. Completely at 1560°. Heated with Fe, Sn, Sb, Cu, Zn &c. a metallic sulphide and Hg is formed.
S attracts Hg
1. less strongly than Cd,
2. less strongly than Ti,
3. more strongly than Au.

Tl and S. [S^{1/2}, Tl] = 10,830.
Tl₂S and Tl₂S₃ have been isolated. Tl₂S₃ is formed when Tl is heated with excess of S. Tl₂S when Tl and S are heated together in the ratio Tl₂:S. Tl₂S is a solid, which when strongly heated melts.
Moist precipitated Tl₂S oxidises in air to Tl₂SO₄. On long continued heating Tl₂S is completely decomposed.
Tl attracts S
1. less strongly than In?
2. more strongly than Pb,
3. more strongly than Hg.

Pb and S.
Pb can be obtained by heating Pb + S, by PbO + S, or H₂S + Pb salt. Melts at a full red heat out of contact with air, and is said to sublime unchanged. Heated in air evolves SO₂ and forms Pb + PbSO₄ + PbO. Heated with PbO forms Pb + SO₂. Melted with scrap iron, FeS + Pb are produced. Heated in steam gives H₂S + PbO at first; then Pb.
S attracts Pb
1. less strongly than Sn,
2. more strongly than Bi,
3. less strongly than Ti.

Bi and S.
Bi₂S₃. Formed Bi + S heated together, also H₂S + solution of Bi salt.
Solid. Strongly heated it separates into Bi and S. Unacted on by alkalis and alkali carbonates.
Bi₂S₃. 2H₂O. Black powder. Decomposed by heating into Bi + Bi₂S₃. By HCl into BiCl₃, Bi and H₂S.
Attempts to prepare Bi₂S₃ have failed. Bi seems to have but a feeble affinity for S.
S attracts Bi
1. less strongly than Sb,
2. less strongly than Pb.



Longitudinal Sections.

H, Li, Na, Cu, Ag, Au. The affinity increases rapidly as we pass from H to Li and then seems to steadily decrease as we pass towards A.

H 1; Li 5; Na 5; Cu 3; Ag 0.5; Au 0.5.

B, Al, Ga, In, Tl. So far as can be judged, the affinity seems to increase as we pass from B to Al, and then probably decreases until Tl is reached.

B 3; Al 3; Ga 3; In 2; Tl 0.5.

C, Si, Ge, Sn, Pb. C and Si have a very feeble affinity for P, Sn has a greater affinity. Pb also seems to have but a feeble affinity.

C 1; Si 1; G 2; Sn 2; Pb 0.5.

N, P, As, Sb, Bi. N has a very considerable affinity for N, and the affinity sinks from N to Bi, being very small at the latter point.

N 12; P 7; As 1; Sb 0.5; Bi 0.5.

O, S, Se, Te. O has a great affinity for P, and the affinity sinks steadily until Te is reached.

O 9.25; S 4.0; Se 3.5; Te 2.0.

F, Cl, Br I. The affinity for P for all these elements is great sinking from F to I.

F 8.5; Cl 6.25; Br 4.15; I 2.5.

Sulphur.

Longitudinal Sections.

Li, Be, B, C, N, P, F. The affinity of Li for S is considerable, but the affinity steadily decreases as we pass towards N, being very small here; it then increases again until F is reached.

H 0.6; Li 14.5; Be 7.5; B 3.45; C 0.5; N 0.2; O 9; F 9.

Na, Mg, Al, Si, P, S, Cl. The affinity for S is considerable at Na, it then sinks until Si is reached, then rises at P, then seems to fall, becoming very small at Cl.

Na 14; Mg 5; Al 3; Si 1.25; P 8; S 5; Cl 1.9.

Cu, Zn, Ga, Ge, As, Se, Br. Cu has a strong affinity for S, and the affinity seems to sink steadily until Br is reached.

Cu 5; Zn 4.6; Ga 4.4; Ge 4.0; As 38; Se 0.6; Br 0.4.

Ag, Cd, In, Sn, Sb, Te, I. Ag has but a feeble affinity for S. The affinity seems to increase considerably as we pass from Ag to Cd, and then very slowly decreases until In is reached, becoming very small at Te, and somewhat greater at I.

Ag 0.6; Cd 4.3; In 4.35; Sn 3.9; Sb 3.7; Te 0.5; I 1.35.

Au, Hg, Tl, Pb, Bi. Au has a feeble affinity for S, and the affinity slowly increases as we pass from Au towards Pb, attaining its greatest value at Pb, and declining somewhat from Pb to Bi.

Au 0.4; Hg 1.0; Tl 2.7; Pb 3.6; Bi 3.5.

Longitudinal.

H, Li Na, Cu, Ag, Au. The attraction for S is small at H, it then increases, being very great at Li and Na, it then rapidly declines, being very small at Au.

H 0.6; Li 14.5; Na 14.0; Cu 5.0; Ag 0.6; Au 0.4.

Be, Mg, Zn, Cd, Hg. The affinity for S does not seem very great for B, and seems to first rise and then fall as we pass down the group of elements, being smallest at Tl.

B 3.45; Al 3.0; Ga 4.4; In 4.35; Tl 2.7.

C, Si, Ge, Sn, Pb. C has but a feeble affinity for S; the affinity seeming to increase up to Ge, and then declines somewhat to Pb.

C 0.5; Si 1.25; Ge 4.0; Sn 3.9; Pb 3.6.

N, P, As, Sb, Bi. The affinity for S is very small at N, and increases very rapidly as we pass from O to P, thereafter slowly declining.

N 0.2; P 8.0; As 38; Sb 3.7; Bi 3.5.

O, S, Se, Te. O has a great affinity for S, the affinity sinking from O to Te.

O 9; S 5; Se 0.6; Te 0.5.

F, Cl, Br, I. The affinity is great at F and decreases from F to I.

F 9.0; Cl 1.9; Br 0.4; I 1.35.

[H, Cl] = 22,000.

H and Cl combine together explosively to form HCl. HCl decompose to H and Cl at 1500°.

Data for determining the force with which the various elements of the primary system A attract Chlorine.

<p>[Cl]. [Li, Cl] = 94,000.</p> <p>Partially decomposed on heating in air, with evolution of Cl. Evaporation of LiClAq is accompanied by slight decomposition. Completely decomposed by heating in steam, with evolution of Cl.</p> <p>Li attracts Cl</p> <ol style="list-style-type: none"> 1. more strongly than H, 2. less strongly than Na, 3. more strongly than Be. 	<p>BeCl₂. [Be^{1/2}, Cl] = 77,500.</p> <p>Not decomposed in absence of air at 1500°. Readily decomposed by heating in air or O to BeO and Cl. Also decomposed by evaporation in water. Be seems to attract Cl</p> <ol style="list-style-type: none"> 1. less strongly than Li, 2. more strongly than B, 3. less strongly than MgCl₂. 	<p>BCl₃. [B^{1/3}, Cl] = 77,500.</p> <p>Fumes in air with decomposition. Is decomposed by water to H₂BO₃. Is not decomposed by heating with Zn dust to 2000°; or with Na below 150°. At 150° B separates.</p> <p>Cl attracts B</p> <ol style="list-style-type: none"> 1. less strongly than Be, 2. more strongly than C, 3. less strongly than Al. 	<p>CCl₄. [C^{1/4}, Cl] = 13,500.</p> <p>Passed through a hot tube decomposes to C₂Cl₂, C₂Cl₆ &c. and hence is not a very stable body.</p> <p>Cl attracts C</p> <ol style="list-style-type: none"> 1. less strongly than B, 2. more strongly than N, 3. less strongly than S. 	<p>NCI₃. [N^{1/3}, Cl] = -13,000.</p> <p>Extremely unstable explosive body. Decomposes when heated to 90°. Explodes in light, contact with organic matter &c.</p> <p>Cl attracts N</p> <ol style="list-style-type: none"> 1. much less strongly than C, 2. less strongly than O, 3. much less strongly than P. 	<p>OCI₂. [O^{1/2}, Cl] = -9,000.</p> <p>Extremely unstable explosive body. OCl₂ is, however, more stable than NCl₃.</p> <p>Cl attracts O</p> <ol style="list-style-type: none"> 1. more strongly than N, 2. more strongly than F? 3. less strongly than S. 	<p>FCI.</p> <p>Unknown. F seems to have but a very feeble affinity for Cl.</p>
<p>NaCl. [Na, Cl] = 98,000.</p> <p>Partially decomposed at a white heat (temperature at which it volatilises). Is decomposed only very slightly indeed by heating in steam or air.</p> <p>Cl attracts Na</p> <ol style="list-style-type: none"> 1. more strongly than Li, 2. more strongly than Cu, 3. more strongly than Mg. 	<p>MgCl₂.</p> <p>Can be distilled in H at a red heat without decomposition. MgCl₂ is partially decomposed by H₂O to MgO + HCl.</p> <p>Cl attracts Mg</p> <ol style="list-style-type: none"> 1. more strongly than Be, 2. more strongly than Zn, 3. less strongly than Na, 	<p>AlCl₃. [Al^{1/3}, Cl] = 54,000.</p> <p>Fumes in moist air, giving off HCl and absorbing H₂O. Easily decomposed (to Al₂O₃ + HCl) by steam. Partially decomposed by O at a red heat, evolving Cl. Decomposed below a red heat by K or Na with production of Al. Undecomposed in N at 1500°.</p> <p>Al attracts Cl</p> <ol style="list-style-type: none"> 1. more strongly than B, 2. more strongly than Ga, 3. less strongly than Mg, 4. more strongly than Si. 	<p>SiCl₄. [Si^{1/4}, Cl] = 39,000.</p> <p>Is capable of existing at a bright red heat, since it is formed by heating SiO₂ and C in a current of Cl at a bright red heat. SiCl₄ is decomposed by passing the vapour mixed with air through a white hot tube. Many metals, eg. K, Na, Zn, Ag &c. withdraw all the Cl from SiCl₄ when heated to redness in vapour of SiCl₄. Heated to redness with H a little CHCl₃ is formed.</p> <p>Cl attracts Si</p> <ol style="list-style-type: none"> 1. more strongly than C, 2. more strongly than Ge, 3. less strongly than Al, 4. more strongly than P. 	<p>PCl₃. [P^{1/3}, Cl] = 25,000.</p> <p>Decomposed by moist air, or H₂O, to HCl and H₃PO₃.</p> <p>Cl attracts P</p> <ol style="list-style-type: none"> 1. much more strongly than N, 2. more strongly than As, 3. less strongly than Si, 4. more strongly than S. 	<p>SCL₂. [S^{1/2}, Cl] = less than +6,000.</p> <p>Very unstable body, easily decomposes to S₂Cl₂ and Cl. At 86° 50% of SCL₂ is thus decomposed.</p> <p>Cl attracts S</p> <ol style="list-style-type: none"> 1. more strongly than O, 2. less strongly than P, 3. less strongly than Se. 	<p>CCl.</p> <p>Cl₂ is stable at ordinary temperatures. But at 1200° it begins to decompose into Cl atoms.</p> <p>Hence Cl₂ is very much more stable than either FCl or BrCl; indeed more stable than SCL₂.</p>
<p>Cu₂Cl₂. [Cu, Cl] = 33,000.</p> <p>Undecomposed at 1560°, having at this temperature the mol. wt. Cu₂Cl₂. Heated in O or water, CuO is formed. Reduced to Cu by heating with H, or by contact with Fe.</p> <p>Cl attracts Cu</p> <ol style="list-style-type: none"> 1. less strongly than Na, 2. more strongly than Ag, 3. less strongly than Zn. 	<p>ZnCl₂. [Zn^{1/2}, Cl] = 49,000.</p> <p>Is stable at 900°, vapour density corresponding to ZnCl₂. Aqueous solution is partially decomposed on evaporation giving oxyhalides.</p> <p>Cl attracts Zn</p> <ol style="list-style-type: none"> 1. less strongly than Mg, 2. more strongly than Cd, 3. much more strongly than Cu, 4. more strongly than Ga. 	<p>GaCl₃.</p> <p>Begins to decompose towards 1100° C giving Cl + GaCl₂. Water partially decomposes it.</p> <p>Cl attracts Ga</p> <ol style="list-style-type: none"> 1. less strongly than Al, 2. more strongly than In, 3. less strongly than Mg, 4. more strongly than Si. 	<p>GeCl₄.</p> <p>Liquid, which fumes in air and is decomposed by water with production of GeO₂. Partially reduced to Ge by heating in H. Formed by heating Ge in Cl.</p> <p>Cl attracts Ge</p> <ol style="list-style-type: none"> 1. less strongly than Si, 2. more strongly than Sn, 3. less strongly than Ga, 4. more strongly than As. 	<p>AsCl₃. [As^{1/3}, Cl] = 24,000.</p> <p>Decomposed by water to oxides and oxy-chlorides.</p> <p>Cl attracts As</p> <ol style="list-style-type: none"> 1. less strongly than P, 2. less strongly than Sb, 3. less strongly than Ge, 4. more strongly than Se. 	<p>SeCl₄. ^{1/4}[Se, Cl] = 11,500 [Se, Cl] = 11,000</p> <p>SeCl₄ is unknown. SeCl₄ and SeCl₂ are known and appear to be fairly stable bodies.</p> <p>Cl attracts Se</p> <ol style="list-style-type: none"> 1. more strongly than S, 2. less strongly than Te, 3. less strongly than As, 4. more strongly than Br. 	<p>BrCl.</p> <p>Is a very unstable body, decomposing about 10° evolving Cl.</p> <p>BrCl is very much less stable than SeCl₄, and seems much less stable than ICl.</p>
<p>Ag, Cl. [Ag, Cl] = 29,000</p> <p>Undecomposed at 1700°, vap. den. at this temp corresponding to AgCl. AgCl is reduced to Ag by many metals e.g., Zn or Fe in the presence of acids. Cu pp's Ag from AgCl in the presence of ammonia. Heated in H or with C, AgCl is reduced to Ag. Cl attracts Ag.</p> <ol style="list-style-type: none"> 1. less strongly than Cu 2. more strongly than Au 3. less strongly than Cd. 	<p>CdCl₂. [Cd^{1/2}, Cl] = 47,000</p> <p>Seems to be a stable body, since it is obtained by heating CdCl₂.2H₂O to low redness. Cd seems to attract Cl.</p> <ol style="list-style-type: none"> 1. more strongly than Ag 2. more strongly than In 4. less strongly than Zn 4. more strongly than Hg 	<p>InCl₃.</p> <p>Towards 1000° InCl₃ begins to dissociate into InCl and Cl. The solution in H₂O may be evaporated almost unchanged in a steam bath, but at higher temps. decomposition occurs with production of oxy-chlorides.</p> <p>Cl attracts In</p> <ol style="list-style-type: none"> 1. less strongly than Ga 2. more strongly than Tl 3. less strongly than Cd 4. more strongly than Sn 	<p>SnCl₄. [Sn^{1/4}, Cl] = 32,000</p> <p>Formed by heating Cl with Sn. A solution of SnCl₄ in H₂O gradually decomposes, giving HCl and SnO₂. Heated in a sealed tube with a little H₂O gives SnO₂.</p> <p>Cl attracts Sn</p> <ol style="list-style-type: none"> 1. less strongly than Ge 2. more strongly than Pb 3. less strongly than In 4. more strongly than Sb 	<p>SbCl₃. [Sb^{1/3}, Cl] = 30,460</p> <p>Prepared by heating Sb in a current of Cl. Dissolved unchanged in a very little H₂O, but with more water SbOCl is produced.</p> <p>Cl attracts Sb</p> <ol style="list-style-type: none"> 1. more strongly than As 2. as strongly as Bi 3. less strongly than Sn 4. more strongly than Te 	<p>TeCl₂.</p> <p>TeCl₂ is stable at 440°, possessing a vapour density corresponding to TeCl₂. The vapour is decomposed by air or O into oxy-chlorides.</p> <p>Cl attracts Te</p> <ol style="list-style-type: none"> 1. more strongly than Se 2. less strongly than Sb 3. more strongly than I. 	<p>ICl. [I, Cl] = 6,700</p> <p>Is not a very stable body, but can be distilled without decomposition. ICl is much more stable than BrCl, but is less stable than TeCl₂. It is less stable than Cl₂.</p>
<p>AuCl. [Au, Cl] = 6,000</p> <p>Unstable body. Heated to 230° decomposes to Au and Cl.</p> <p>Cl attracts Au</p> <ol style="list-style-type: none"> 1. less strongly than Ag 2. less strongly than Hg 	<p>HgCl₂. [Hg^{1/2}, Cl] = 27,000</p> <p>Fairly stable under action of heat. May be volatilised without decomposition; can be fairly easily decomposed by various metals, such as Cu, Sb, As, Bi, Pb, Ni, Sn, Fe &c.</p> <p>Cl attracts Hg</p> <ol style="list-style-type: none"> 1. more strongly than Au 2. less strongly than Tl 3. less strongly than Cd. 	<p>TlCl. [Tl, Cl] = 48,6000</p> <p>TlCl is a stable body; TlCl₃ unstable, easily decomposing.</p> <p>Cl attracts Tl</p> <ol style="list-style-type: none"> 1. less strongly than In 2. more strongly than Hg 3. more strongly than Pb 	<p>PbCl₂. [Pb^{1/2}, Cl] = 43,900</p> <p>PbCl₂ is a very stable body; PbCl₄ on the other hand is very unstable.</p> <p>Cl attracts Pb</p> <ol style="list-style-type: none"> 1. less strongly than Sn 2. less strongly than Tl 3. more strongly than Bi 	<p>BiCl₃. [Bi^{1/3}, Cl] = 30,210</p> <p>BiCl₃ boils unchanged at 249°. Is decomposed by water to BiOCl + HCl. Heated in H is reduced first to BiCl₂ and then to Bi.</p> <p>Cl attracts Bi</p> <ol style="list-style-type: none"> 1. less strongly than Sb (a little) 2. less strongly than Pb 		

No.	Name of the	Address
1	J. H. Smith	123 Main St.
2	W. B. Jones	456 Elm St.
3	C. D. Brown	789 Oak St.
4	A. E. White	101 Pine St.
5	M. L. Green	234 Cedar St.
6	R. T. Black	567 Birch St.
7	S. P. Gray	890 Spruce St.
8	D. K. Hall	1122 Ash St.
9	F. G. Young	1444 Willow St.
10	H. J. King	1777 Poplar St.
11	L. A. Scott	2000 Magnolia St.
12	N. M. Adams	2333 Sycamore St.
13	O. P. Baker	2666 Chestnut St.
14	Q. R. Carter	2999 Walnut St.
15	T. S. Evans	3333 Hickory St.
16	U. V. Fisher	3666 Dogwood St.
17	V. W. Gibson	3999 Redwood St.
18	W. X. Hart	4333 Cypress St.
19	X. Y. Lane	4666 Juniper St.
20	Y. Z. Miller	4999 Fir St.
21	Z. A. Nelson	5333 Hemlock St.
22	A. B. Phillips	5666 Larch St.
23	B. C. Quinn	5999 Locust St.
24	C. D. Reed	6333 Maple St.
25	D. E. Stiles	6666 Palm St.
26	E. F. Taylor	6999 Peach St.
27	F. G. Underhill	7333 Plum St.
28	G. H. Vance	7666 Rose St.
29	H. I. Webb	7999 Strawberry St.
30	I. J. Wright	8333 Tangerine St.

Chlorine

Longitudinal Sections.

H, Li, Na, Cu, Ag, Au. The attraction for chlorine is great at H, becomes very great at Li and Na and then decreases rapidly up to Au.

H 5.5; Li 23.5; Na 24.5; Cu 8.25; Ag 7.25; Au 1.50.

Be, Mg, Zn, Cd, Hg. The attraction for Cl is great at Be and falls steadily from Be to Hg.

B 19.4; Mg 19.0; Zn 12.25; Cd 11.7; Hg 7.0.

B, Al, Ga, In, Tl. The attraction for Cl rises from B to Al and then falls.

B 9.0; Al 13.5; Ga 10.0; In 9.5, I 4.

C, Si, Ge, Sn, Pb. The affinity from chlorine rises from C to Si, and then decreases as we go towards Pb.

C 3.4; Si 9.7; Ge 8.0; Sn 8.0; Pb 3.

N, P, As, Sb, Bi. The attraction for Cl is very small for N, rises considerably up to P, falls very slightly for As, then rises again for Sb, remains about the same (perhaps a shade less) for Bi.

N 0.1; P 6.25; As 6.0; Sb 7.6; Bi 7.5.

O, S, Se, Te. The attraction is small for O and rises steadily up to Te.

O 0.2; S 1; Se 2.8; Te 4.0.

F, Cl, Br, I. The attraction for Cl is feeble for all, rising from F to Cl, sinking from Cl to Br, and rising again at I.

F 0.2; Cl 5.0; Br 0.5; I 1.7.

Cross Sections.

Li, Be, B, C, N, O, F. The attraction for Cl is very great at Li, but sinks as we pass towards F, being very small at this element.

Li 23.5; Be 19.4; B 9.0; C 3.4; N 0.1; O 0.2; F 0.2.

Na, Mg, Al, Si, P, S, Cl. The attraction for Cl is very great at Na, sinks as we pass from Na towards S, becoming very small at S, and rising slightly at Cl.

Na 24.5; Mg 19; Al 13.5; Si 9.7; P 6.25; S 1.0; Cl 5.0.

Cu, Zn, Ga, Ge, As, Se, Br. The attraction for Cl rises up from Cu to Zn, and then steadily decreases to Br, where it becomes very small.

Cu 8.25; Zn 12.25; Ga 10; Ge 8; As 6; Se 2.8; Br 0.5

Ag, Cd, In, Sn, Sb, Te, I. Ag has a considerable attraction for Cl, the attraction rises steadily from Ag to Cd, and then falling as we go towards I, where it is very small.

Ag 7.25; Cd 11.7; In 9.5; Sn 8.0; Sb 7.6; Te 4; I 1.7.

Au, Hg, Tl, Pb, Bi. The affinity of Au for S is very feeble, the affinity rising as we pass from Au to Hg, and remains great throughout the series.

Au 1.5; Hg 7.0; Tl 4.0; Pb 3; Bi 2?

P o t a s s i u m

Longitudinal Sections.

F, Cl, Br, I. The attraction for K is very great for all these elements, falling slowly as we pass from Cl to I.

F 25.0; Cl 26.4; Br 23.8; I 20.1.

O, S, Se, Te. The attraction for K seems to rise somewhat as we pass from O to S, for Se it is a very little greater than for O, judging from thermal data.

O 2.9; S 12.0; Se 12.25.

N, P, As, Sb, Bi. The attraction of N for K is feeble, P attracts it with a greater force; and probably As with a force greater than P. Sb and Bi also combine with K.

N 0.5; P 4.5; As 5.0; Sb 2.5; Bi 2.6.

C, Si, Ge, Sn, Pb. All these elements have probably but a feeble affinity for K.

C 0.4; Si 0.3; Ge 0.3; Sn 0.3; Pb 2.3.

B, Al, Ga, In, Tl. All these elements have but a feeble affinity for K.

B 0.5; Al 0.5; Ga 0.3; In 0.3; Tl 2.0.

Be, Mg, Zn, Cd, Hg. All except Hg seem to have but a feeble affinity for K. Hg however combines with K with the evolution of much heat.

Be 0.5; Mg 0.5; Zn 0.5; Cd 0.5; Hg 8.5.

H, L, Na, Cu, Ag, Au. All have but a very feeble affinity for K.

H 4.0; Li 0.5; Na 0.5; Cu 0.5; Ag 0.5; Au 0.5.

Cross Sections.

Li, Be, B, C, N, O, F, Ne. So far as can be judged, the attraction for K is very small for Li and seems to rise steadily until C is reached, it then falls slightly for N, and then rapidly rises to F.

Li 0.5; Be 0.5; B 0.5; C 0.6; N 0.5; O 2.9; F 25.0.

Na, Mg, Al, P, S, Cl, Ar. The attraction is small for N and rises steadily until Cl is reached.

Na 0.5; Mg 0.5; Al 0.5; P 4.5; S 12.0; Cl 26.4.

Cu, Zn, Ga, Ge, As, Se, Br. The attraction is small for Cu and rises steadily until Br is reached.

Cu 0.5; Zn 0.5; Ga 0.3; Ge 0.3; As 5.0; Se 12.2; Br 23.8.

Ag, Cd, In, Sn, Sb, Te, I. The affinity rises steadily from Ag to I, being small for Ag and great for I.

Au, Hg, Tl, Pb, Bi. The affinity for K of Au is feeble, of Hg great. Tl, Pb, Bi small but perceptible..

Au 0.5; Hg 8.5; Tl 3.0; Pb 2.3; Bi 2.0.

Copper.

Cross Sections.

Li, Be, B, C, N, O, F. From Li to N the elements have all very feeble affinities for Cu; the affinity, however, becomes very great at O and still greater at F.

Li 0.5; Be 0.5; B 1.5; C 1.5; N 0.5; O 5.1; F 7.0.

Na, Mg, Al, Si, P, S, Cl. The first three elements have but very feeble affinities for Cu; then the affinity increases, becoming considerable at S and very great at Cl.

Na 0.5; Mg 0.5; Al 1.0; Si 2.0; P 2.0; S 4.0; Cl 8.25.

Cu, Zn, Ga, Ge, As, Se, Br. Up to Ge the affinity is feeble, it then rises, becoming considerable at Se and great at Br.

Cu 0.5; Zn 0.5; Ga 0.5; Ge 1.0; As 1.5; Se 2.6; Br 6.25.

Ag, Cd, In, Sn, Sb, Te, I. Up to Sb all have a very feeble affinity for Cu; Te has a considerable and I a great affinity.

Ag 0.5; Cd 0.5; In 0.5; Sn 1.0; Sb 1.0; Te 1.8; I 4.4.

Au, Hg, Tl, Pb, Bi. All these elements have but a very feeble affinity for Cu.

Au 0.5; Hg 0.5; Tl 0.5; Pb 0.5; Bi 0.5.

Longitudinal Sections.

H, Li, Na, Cu, Ag, Au. All these elements have but a very feeble affinity for Cu.

H 0.5; Li 0.5; Na 0.5; Cu 0.5; Ag 0.5.

Be, Mg, Zn, Cd, Hg. All have but a feeble affinity for copper.

Be 0.5; Mg 0.5; Zn 0.5; Cd 0.5; In 0.5; Tl 0.5.

B, Al, Ga, In, Tl. All have but a feeble affinity for Cu.

B 1.0; Al 1.0; Ga 0.5; In 0.5; Tl 0.5.

C, Si, Ge, Sn, Pb. All these elements have a feeble but perceptible affinity for Cu, the affinity rising as we pass from C to Si, and is very appreciable at Sn, and less for Pb.

N, P, As, Sb, Bi. The affinity is feeble for all these elements, seeming to rise as we pass from N to P and thereafter to sink.

N 0.5; P 2; As 1.5; Sb 0.5; Bi 0.5.

O, S, Se, Te. The affinity is great at O and steadily decreases as we proceed from O to Te.

O 5.1; S 4.0; Se 2.6; Te 1.8.

F, Cl, Br, I. The affinity is considerable for F and increases as we pass from F to Cl, and then decreases until I is reached, but remains considerable even at I.

F 7.0; Cl 8.85; Br 6.25; I 4.4.

Z i n c.

Longitudinal Sections.

H, Li, Na, Cu, Ag, Au. All these bodies seem to have but a very feeble affinity for Zn.

H 0.5; Li 0.5; Na 0.5; Cu 0.5; Ag 0.5; Au 0.5.

Be, Mg, Zn, Cd, Hg. Affinity feeble for all.

B 0.5; Mg 0.5; Zn 0.5; Cd 0.5; Hg 0.5.

B, Al, Ga, In, Tl. Affinity feeble for all.

B 0.5; Al 0.5; Ga 0.5; In 0.5; Tl 0.5.

C, Si, Ge, Sn, Pb. All these elements have a small but appreciable affinity for Zn.

C 0.8; Si 0.8; Ge 0.5; Sn 0.5; Pb 0.5.

N, P, As, Sb, Bi. N, P, As have all appreciable affinities for Zn, the affinity increasing somewhat as we pass from N to P and then decreasing from P to As. Sb and Bi have but feeble affinities.

N 2; P 2.5; As 2; Sb 0.5; Bi 0.5.

O, S, Se, Te. All these elements have a great affinity for Zn, the affinity steadily decreasing as we pass from O to Te.

O 10.7; S 5.2; Se 5.0; Te 4.6.

F, Cl, Br, I. The attraction for all these elements is very great decreasing as we pass from F to I.

F 14.0; Cl 12.25; Br 10.0; I 6.1.

Cross Sections.

Li, Be, B, C, N, O, F. The affinity for Ag is small at Li and rises as we pass towards Cl, becoming appreciable at C and N, great at O, and greatest at F.

Li 0.5; Be 0.5; B 0.5; C 0.8; N 2.0; O 10.7; F 14.0.

Na, Mg, Al, Si, P, S, Cl. The affinity is at first feeble, and rises as we pass towards Cl, becoming great at S, and very great at Cl.

Na 0.5; Mg 0.5; Al 0.5; Si 0.8; P 2.5; S 5.2; Cl 12.25.

Cu, Zn, Ga, Ge, As, Se, Br. Cu and Zn have but feeble affinities, the affinity becomes appreciable at As, great at Se, and very great at Br.

Cu 0.5; Zn 0.5; Ga 0.5; Ge 0.5; As 2.0; Se 5.0; Br 10.0.

Ag, Cd, In, Sn, Sb, Te, I. Up to Sb the affinity is feeble, at Te it becomes considerable, and attains its greatest value at I.

Ag 0.5; Cd 0.5; In 0.5; Sn 0.5; Sb 0.5; Se 4.65; I 6.25.

Au, Hg, Tl, Pb, Bi. All these substances have only exceedingly small affinities for Zn.

Au 0.5; Hg 0.5; Tl 0.5; Pb 0.5; Bi 0.5.

A r s e n i c.

Longitudinal Sections.

H, Li, Na, Cu, Ag, Au. H has a very feeble affinity for As, the affinity rising considerably as we pass from Na to Cu, remaining small until Au is reached.

H 0.5; Li 3.5; Cu 1; Ag 1; Au 1.

Be, Mg, Zn, Cd, Hg. This affinity is considerable for Be and Mg, and sinks as we pass from Be to Hg, being very small at Hg.

Be 2.5; Mg 2.5; Zn 1; Cd 0.8; Hg 0.5.

B, Al, Ga, In, Tl. The affinity for all is feeble, rising from B to Al and sinking at Tl.

B 0.5; Al 2.4; Ga 2?; In 2?; Tl 1.5.

C, Si, Ge, Sn, Pb. The affinity of all for As is feeble, being probably greatest at Sn, and least at C.

C 0.5; Si 0.5; Ge 1.5; Sn 2; Pb 1.5.

N, P, As, Sb, Bi. The affinity for As is very feeble at N, rises thence to As, and then falls to Bi.

N 0.5; P 0.6; As 4; Sb 1; Bi 1.

O, S, Se, Te. O has a very considerable affinity for As, and the attraction seems to decrease steadily until Te is reached.

O 6.4; S 4; Se 3.5; Te 3.

F, Cl, Br, I. F has a great attraction for As, and the attraction decreases steadily as we pass from F to I.

F 7; Cl 6; Br 5; I 2.4.

Cross Sections.

Li, Be, B, C, N, O, F. The attraction for As is considerable at Li; and sinks as we pass from Li to B, remaining very small up to N. At O it becomes great and increases somewhat as we pass from O to F.

Li 3.5; Be 2.5; B 0.5; C 0.5; N 0.5; O 6.4; F 7.

Na, Mg, Al, Si, P, S, Cl. Na has a considerable attraction for As; the attraction seems to diminish as we pass from Na to

Al. At Si and P the attraction is very small and rises rapidly as we pass from P to S, attaining its greatest value at Cl.

Na 3.5; Mg 2.5; Al 2.4; Si 0.5; P 0.6; S 4.0; Cl 6.0.

Cu, Zn, Ga, Ge, As, Se, Br. Cu and Zn have but a very feeble affinity for As; the attraction increases as we pass from Zn to Br, attaining its greatest value at Br.

Ag, Cd, In, Sn, Sb, Te, I. Ag, Cd, Sn, Sb have all perceptible but feeble affinities for As; Te and I have greater affinities.

Ag 1.0; Cd 0.8; In 2.0; Sn 2.0; Sb 1.0; Te 3.0; I 2.4.

Au, Hg, Tl, Pb, Bi. All these elements have but a very feeble affinity for As.

Au 1.0; Hg 0.5; Tl 1.5; Pb 1.5; Bi 1.

S e l e n i u m.

Longitudinal Sections.

H, Li, Na, Cu, Ag, Au. The affinity for Se is small at H, and rises as we pass from H to Li or Na, being great here, it then sinks, being small at Au.

H 0.2; Li 11.3; Na 11.4; Cu 2.6; Ag 0.6; Au 0.5.

Be, Mg, Zn, Cd, Hg. The attraction steadily decreases as we pass from Be to Hg, but is great for all these bodies.

Be 8; Mg 7.5; Zn 5; Cd 3.0; Hg 2.5.

B, Al, Ga, In, Tl. All these elements seem to have a considerable affinity for Se, the affinity sinking as we pass from B to Tl.

B 7; Al 6; Ga 4.5; In 3.5; Tl 2.2;

C, Si, Ge, Sn, Pb. C and Si seem to have but feeble affinities for Se, and the affinity steadily rises as we pass from C to Sn, it probably sinks somewhat as we pass from Sn to Pb, but remains great for the latter element.

C 0.5; Si 0.5; Ge 3.0; Sn 3.9; Pb 3.4.

N, P, As, Sb, Bi. The affinity for Se is very small at N, and increases as we proceed down the group, becoming greatest at Sb and decreasing slightly as we pass from Sb to Bi.

N 0.5; P 2.5; As 3; Sb 3.5; Bi 3.3.

O, S, Se, Te. O has a great affinity for Se, and the attraction for Se sinks to a very low value as we pass from O to S. At Se again the attraction rises greatly — Se atoms having a great tendency to associate together — and finally sinks again at Te to a small value.

O 7.1; S 0.5; Se 5.3; Te 1.5.

F, Cl, Br, I. The attraction for Se is great at F, and steadily sinks from F to I, being small at I.

F 7.5; Cl 3.0; Br 2.5; I 2.0.

Cross Sections.

Li, Be, B, C, N, O, F. The affinity decreases steadily as we pass from Li to B, and becomes very small at C and N; it then rises becoming great at O and somewhat greater at F.

Li 10; Be 8; B 7; C 0.5; N 0.5; O 7; F 7.5.

Na, Mg, Al, Si, P, S, Cl. The affinity is great for Na and steadily decreases until Si is reached. It then rises again at P, sinks again at S, and then rises to a considerable extent at Cl.

Na 10; Mg 7; Al 6; Si 0.5; P 2.5; S 0.5; Cl 5.0.

Cu, Zn, Ga, Ge, As, Se, Br. The affinity rises considerably as we pass from Cu to Zn, but seems to be fairly great for all these elements.

Cu 3.7; Zn 4.6; Ga 5.0; Ge 3.0; As 3.0; Se 3.0; Se 5; Br 3.5.

Ag, Cd, In, Sn, Sb, Te, I. The affinity rises greatly as we pass from Ag to Cd, and remains great up to Sb. At Te a decrease takes place, followed by a rise at I.

Ag 2.5; Cd 4; In 4; Sn 3.8; Sb 3.5; Te 1.5; I 2.0.

Au, Hg, Tl, Pb, Bi. The affinity is feeble at Au, and rises considerably as we pass from Au up to Hg, it then falls slowly up to Bi, but remains considerable even at Bi.

Au 1.0; Hg 3.7; Tl 3.5; Pb 3.4; Bi 3.3.

B r o m i n e.

Longitudinal Sections.

H, Li, Na, Cu, Ag, Au. H has a considerable affinity for Br, and the affinity increases greatly as we pass from H to Li,

and slightly from Li to Na — being very great at Na. It then drops from Na to Cu and becomes small at Au.

H 2.1; Li 20; Na 21.5; Cu 6.25; Ag 5.5; Au 0.7.

Be, Mg, Zn, Cd, Hg. All these elements have a considerable affinity B for Br, the affinity sinking from Be to Hg.

Be 17; Mg 16.5; Zn 10.0; Cd 9.5; Hg 6.1.

B, Al, Ga, In, Tl. The affinity rises from B to Al, and then sinks until Tl is reached.

B 7.0; Al 10.25; Ga 9.0; In 8.5; Tl 5.0.

C, Si, Ge, Sn, Pb. The affinity is feeble for C, and increases as we pass from C to Sn, and then decreases somewhat from Sn to Pb.

C 3.0; Si 7.5; Ge 8.0; Sn 8.0; Pb 3.0.

N, P, As, Sb, Bi. N has a very feeble affinity for Br, and the affinity rises steadily up to Sb, being about equal for Sb and Bi.

N 0.1; P 4.15; As 5.0; Sb 6.4; Bi 6.25.

O, S, Se, Te. O and S have exceedingly small affinities for Cl, the attraction increasing as we proceed towards Te.

O 0.2; S 0.3; Se 2.0; Te 3.5.

F, Cl, Br, I. F and Cl have but feeble affinities for Br; and so has I.

F 1.5; Cl 0.5; Br 5.0; I 0.8.

Cross Sections.

Li, Be, B, C, N, O, F. The affinity for Br is very great at Li, and sinks rapidly as we pass from Li to N, where it becomes very small indeed; it remains very small at O, and then rises somewhat as we pass from O to F.

Na, Mg, Al, Si, P, S, Cl. The affinity is very great for Na, and sinks steadily until S is reached, where it is very small, and then rises somewhat at Cl.

Na 21.5; Mg 16.5; Al 10.25; Si 7.5; P 4.15; S 0.3; Cl 0.5.

Cu, In, Ga, Ge, As, Se, Br. Cu has a considerable affinity for Br, and the affinity increases greatly as we pass from Cu to Zn, then decreases, becoming small at Se, and rising again at Br.

Cu 6.25; Zn 10.0; Ga 9; Ge 8; As 5; Se 2; Br 5.

Ag, Cd, In, Sn, Sb, Te, I. Ag has a great affinity for Br, the affinity rising for Cd, and then steadily sinking up to I, where it is feeble.

Ag 5.5; Cd 9.5; In 8.5; Sn 8.0; Sb 6.4; Te 3.5; I 0.8.

Au, Hg, Tl, Pb, Bi. Au has but a feeble affinity for Br, the affinity rising greatly at Hg, and remaining great up to Bi.

Au 0.7; Hg 6.1; Tl 5.0; Pb 3.0; Bi 6.25.

Silver.

Longitudinal Sections.

H, Li, Na, Cu, Ag, Au. All these substances have an excessively feeble affinity for Ag.

H 0.2; Li 0.3; Na 0.3; Cu 0.2; Ag 0.2; Au 0.2.

Be, Mg, Zn, Cd, Hg. All have but a very feeble affinity for Cu.

Be 0.2; Mg 0.2; Zn 0.2; Cd 0.2; Hg 0.2.

B, Al, Ga, In, Tl. Affinity very feeble for all.

B 0.2; Al 0.2; Ga 0.2; In 0.2; Tl 0.2.

C, Si, Ge, Sn, Pb. All these elements have but a very feeble affinity for Ag.

C 0.2; Si 0.2; Ge 0.2; Sn 0.2; Pb 0.2.

N, P, As, Sb, Bi. The affinity for Ag of all these elements from N to Bi is small. It rises as we pass from N to P, and then falls up to Bi.

N 0.2; P 0.5; As 0.4; Sb 0.3; Bi 0.2.

O, S, Se, Te. O has but a feeble affinity for Ag, and the affinity decreases as we pass from O to Te.

O 0.8; S 0.7; Se 0.6; Te 0.5.

F, Cl, Br, I. F possesses a feeble affinity for Ag, the affinity rising considerably as we pass from F to Cl, being great at this element. It then slowly decreases until I is reached, but still remains considerable here.

F 3.0; Cl 7.25; Br 5.5; I 3.5.

Cross Sections.

Li, Be, B, C, N, O, F. The affinity for Ag is very small up to N; At O it becomes appreciable, but is still small; At F it is somewhat greater.

Li 0.2; Be 0.2; B 0.2; C 0.2; N 0.2; O 0.2; F 3.0.

Na, Mg, Al, Si, P, S, Cl. The affinity for Ag is very small up to Si; At P it becomes appreciable, rises somewhat as we pass from P to S, and then largely as we pass from S to Cl.

Na 0.2; Mg 0.2; Al 0.2; Si 0.2; P 0.5; S 0.7; Cl 7.25.

Cu, Zn, Ga, Ge, As, Se, Br. The affinity for Ag is very small up to As, at Se it becomes appreciable and increases thence until I is reached.

Cu 0.2; Zn 0.2; Ga 0.2; Ge 0.2; As 0.4; Se 0.6; Br 5.5.

Ag, Cd, In, Sn, Sb, Te, I. The affinity for Ag is very small up to Sn. At Sb it is small but appreciable, and increases thence until I is reached.

Ag 0.2; Cd 0.2; In 0.2; Sn 0.2; Sb 0.3; Te 0.5; I 3.5.

Au, Hg, Tl, Pb, Bi. All these elements have an excessively feeble affinity for Ag.

Au 0.2; Hg 0.2; Tl 0.2; Pb 0.2; Bi 0.2.

C a d m i u m .

Longitudinal Sections.

H, Li, Na, Cu, Ag, Au. All these elements seem to possess an extremely small affinity for Cd.

H 0.1; Li 0.1; Na 0.1; Cu 0.1; Ag 0.1; Au 0.1.

Be, Mg, Zn, Cd, Hg. All these elements seem to have a very feeble affinity for Cd.

Be 0.1; Mg 0.1; Zn 0.1; Cd 0.1; Hg 0.1.

B, Al, Ga, In, Tl. All have but a very feeble affinity for Cd.

B 0.1; Al 0.1; Ga 0.1; In 0.1; Tl 0.1.

C, Si, Ge, Sn, Pb. All these have but a very feeble affinity for Cd.

C 0.2; Si 0.1; Ge 0.1; Sn 0.1; Pb 0.1.

N, P, As, Sb, Bi. All have but a feeble affinity for Cd, the affinity increasing as we pass from N to P, and then again decreasing until Bi is reached.

N 0.2; P 0.8; As 0.7; Sb 0.1; Bi 0.1.

O, S, Se, Te. The affinity is great for O and decreases steadily as we pass from O towards Te.

O 9.4; S 5.0; Se 3.0; Te 2.5.

F, Cl, Br, I. All these elements have a great affinity for Cd, the affinity decreasing as we pass from Cl towards I.

F 10; Cl 12; Br 9.5; I 6.1.

Cross Sections.

Li, Be, B, C, N, O, F. At Li the affinity for Cd is small, but increases as we pass towards F. The affinity is very great at O, and probably somewhat greater at F.

Li 0.1; Be 0.1; B 0.1; C 0.2; N 0.2; O 9.4; F 10.0.

Na, Mg, Al, Si, P, S, Cl. The affinity is small for Li and Mg but increases as we pass towards Cl, becoming very great at this latter element.

Na 0.1; Mg 0.1; Al 0.1; Si 0.1; P 0.8; S 5.0; Cl 12.0.

Cu, Zn, Ga, Ge, As, Se, Br. The affinity is very small for the first few elements but increases as we pass towards Br, becoming perceptible at As, considerable at As, and great at Br.

Cu 0.1; Zn 0.1; Ga 0.1; Ge 0.1; As 0.7; Se 3.0; Br 9.5.

Ag, Cd, In, Sn, Sb, Te, I. The affinity is very small up to Sb. At Te it becomes perceptible and at I great.

Ag 0.1; Cd 0.1; In 0.1; Sn 0.1; Sb 0.1; Te 2.5; I 6.1.

Au, Hg, Tl, Sb, Bi. The affinity is very small for all these elements.

Au 0.1; Hg 0.1; Tl 0.1; Pb 0.1; Bi 0.1.

Tin.

H, Li, Na, Cu, Ag, Au. H has a very feeble affinity for Sn, and the affinity rises as we pass from H to Li, and sinks again as we pass from Na to Cu. The affinity for Sn is, however, but feeble for all.

H 0.2; Li 1.0; Na 1.0; Cu 0.5; Ag 0.5; Au 0.5.

Be, Mg, Zn, Cd, Hg. All these elements have an excessively feeble affinity for Sn.

Be 0.5; Mg 0.5; Zn 0.5; Cd 0.5; Hg 0.5.

B, Al, Ga, In, Tl. All these elements have only a very feeble affinity for Sn.

B 0.5; Al 0.5; Ga 0.5; In 0.5; Tl 0.5.

C, Si, Ge, Sn, Pb. All these elements have an excessively feeble affinity for Sn.

C 0.5; Si 0.5; Ge 0.5; Sn 0.5; Pb 0.5.

N, P, As, Sb, Bi. N has an exceedingly feeble affinity for Sn, P and As very perceptible affinities, Sb and Bi very small. The affinities increase as we pass from N to P and fall as we pass from P to Sb and Bi.

N 0.1; P 2.0; As 1.0; Sb 0.5; Bi 0.5.

O, S, Se, T. The affinity for Sn is great at O, and sinks steadily until Te is reached.

O 5.8; S 4.5; Se 4.0; Te 3.5.

F, Cl, Br, I. The affinity for Sn is great for all, sinking from F to I.

F 9; Cl 8; Br 7; I 6.

Cross Sections.

Li, Be, B, C, N, O, F. The attraction for Sn is probably feeble for Li and sinks as we pass from Li to Be, it remains small up to N and at O it becomes great, at F still greater.

Li 1.0; Be 0.5; B 0.5; C 0.5; N 0.1; O 5.8; F 9.0.

Na, Mg, Al, Si, P, S, Cl. The affinity is feeble but appreciable at Na and sinks as we pass from Na to Mg. It remains very small up to Si, at P it becomes considerable and hence rises rapidly until it reaches its greatest value at Cl.

Na 1.0; Mg 0.5; Al 0.5; Si 0.5; P 2.0; S 4.5; Cl 8.0.

Cu, Zn, Ga, Ge, As, Se, Br. The affinity for Sn is very small up to Ge, at As it becomes very perceptible, and rises rapidly as we pass onwards, attaining its greatest value at Br.

Cu 0.5; Zn 0.5; Ga 0.5; Ge 0.5; As 2.0; Se 4; Br 7.

Ag, Cd, In, Sn, Sb, Te, I. The affinity for Sn is very feeble until Sb is reached. At Te it becomes considerable and at I great.

Ag 0.5; Cd 0.5; In 0.5; Sn 0.5; Sb 0.5; Te 3.5; I 6.0.

Au, Hg, Tl, Pb, Bi. All these elements have only a very feeble affinity for Sn.

Au 0.5; Hg 0.5; Tl 0.5; Pb 0.5; Bi 0.5.

Antimony.

Longitudinal Sections.

H, Li, Na, Cu, Ag, Au. The affinity for Sb is feeble at H, and rises as we pass from H to Li, and then drops as we pass from Na to Cu, remaining small but appreciable until Au.

H 0.2; Li 2.6; Na 2.6; Cu 0.6; Ag 0.6; Au 0.5.

Be, Mg, Zn, Cd, Hg. Be and Mg have probably very feeble affinities for Sb, Zn, Cd, and Hg still smaller affinities.

Be 0.3; Mg 2.0; Zn 0.5; Cd 0.4; Hg 0.2.

B, Al, Ga, In, Tl. All have a very feeble affinity for Sb.

B 0.5; Al 2; Ga 0.5; In 0.5; Tl 0.5.

C, Si, Ge, Sn, Pb. Affinity of all is feeble.

C 0.5; Si 0.5; Ge 0.5; Sn 0.5; Pb 0.5.

N, P, As, Sb, Bi. All these substances have but a feeble affinity for Sb — the affinity seeming to increase somewhat as we pass from N to As and thereafter probably decreasing.

N 0.5; P 0.6; As 1.0; Sb 0.6; Bi 0.5.

O, S, Se, Te. Sb has a considerable affinity for Sb, and the affinity decreases as we pass from O to Te, but still remains perceptible at Te.

O 7; S 4; Se 3; Te 2.

F, Cl, Br, I. All these elements have a great affinity for Pb, the affinity sinking as we pass from F to I.

F. 8.5; Cl 7.6; Br 6.4; I 3.8.

Cross Sections.

Li, Be, B, C, N, O, F. The affinity for Sb is great at Li, and decreases as we pass from Li to Be; remaining very small

until N is reached. It then rises and at O becomes great and at F somewhat but not much greater.

Li 2.6; Be 0.8; B 0.5; C 0.5; O 7.0; F 8.5.

Na, Mg, Al, Si, P, S, Cl. Na, Mg, Al, have all considerable affinities for Sb; the affinity seeming to sink as we pass from Na to Al. At Si and P the affinity becomes very small. It then rises sharply, becoming considerable at S and great at Cl.

Na 2.6; Mg 2.0; Al 2.0; Si 0.5; P 0.6; S 4.0; Cl 7.6.

Cu, Zn, Ga, Ge, As, Se, Br. Cu, Zn, Ga, Ge, have all but feeble affinities for Sb. At As the affinity becomes appreciable and increases rapidly as we pass towards Se, becoming greatest at Br.

Cu 0.6; Zn 0.5; Ga 0.5; Ge 0.5; As 1.0; Se 3.0; Br 6.4.

Ag, Cd, In, Sn, Sb, Te, I. Up to Sb the affinity is very feeble. At Te it becomes appreciable, and at I still greater.

Ag 0.6; Cd 0.4; In 0.5; Sn 0.5; Sb 0.6; Te 2.0; I 3.8.

Au, Hg, Tl, Pb, Bi. All these elements have only a very feeble affinity for Sb.

Au 0.5; Hg 0.2; Tl 0.5; Pb 0.5; Bi 0.5.

T e l l u r i u m.

Longitudinal Sections.

H, Li, Na, Cu, Ag, Au. The affinity is small for H, rises considerably at Li and Na, and then sinks until Au is reached.

H 0.2; Li 9; Na 9; Cu 2; Ag 0.5; Au 0.4.

Be, Mg, Zn, Cd, Hg. The affinity is probably greatest for Be or Mg, and steadily sinks until Hg is reached.

Be 7.5; Mg 6.5; Zn 4.65; Cd 2.5; Hg 2.0.

B, Al, Ga, In, Tl. The affinity seems to decrease from Al to Tl, being great at Al and considerable at Tl.

B 4; Al 5.5; Ga 3.5; In 2; Tl 1.6.

C, Si, Ge, Sn, Pb. No compounds of C, Si, Ge with Te have been investigated C and Si have probably a very feeble affinity for Te, Sn and Pb have considerable affinities.

C 0.5; Si 0.4; Ge 2; Sn 1.8; Pb 1.43.

N, P, As, Sb, Bi. N has but a feeble affinity for Te; the affinity rises, but still remains feeble at P; As, Sb, Bi seem all to have considerable affinities.

N 0.5; P 1.9; As 2; Sb 1.5; Bi 1.3.

O, S, Se, Te. O has a great affinity for Te; the affinity decreases as we pass from O to S, remaining small for Se and then again for Te.

O 12.2; S 0.5; Se 0.5; Te 4.5.

F, Cl, Br, I. The affinity is great for all these elements and decreases steadily as we pass from F to I.

F 10.5; Cl 9.6; Br 8; I 7.

Cross Sections.

Li, Be, B, C, N, O, F. The affinity is great for Li, and seems to decrease steadily until N is reached, and then rises again, becoming great at O and F.

Li 9; Be 7.5; B 4; C 0.5; N 0.5; O 12.3; F 12.

Na, Mg, Al, Si, P, S, Cl. The affinity decreases steadily as we pass from Na to Al, and becomes small at Si, P and S; it then rises becoming great at Cl.

Na 9; Mg 6.5; Al 5.5; Si 0.5; P 1.9; S 0.5; Cl 9.6.

Cu, Zn, Ga, Ge, As, Se, Br. The affinity is considerable at Cu, and rises as we pass from Cu to Zn, it remains considerable until As is reached; at Se it becomes very small, at Br again rising.

Cu 2; Zn 4.65; Ga 3.5; Ge 2; As 2; Se 0.5; Br 8.

Ag, Cd, In, Sn, Sb, Te, I. Ag has a small affinity for Te, the affinity rising as we pass from Ag to Cd; it then probably decreases somewhat, but at Te again increases, attaining its greatest value at I.

Ag 0.5; Cd 2.5; In 2.0; Sn 1.8; Sb 1.5; Te 4.5; I 7.

Au, Hg, Tl, Pb, Bi. The affinity is feeble at Au, and rises considerably as we pass from Au to Hg and then very slowly decreases until Bi is reached.

Au 0.4; Hg 2; Tl 1.6; Pb 1.43; Bi 1.3.

Iodine.

Longitudinal Sections.

H, Li, Na, Cu, Ag, Au. The affinity for I is small at H, and increases greatly as we pass from H to Na; it then again decreases becoming small at Au.

H 0.5; Li 16.0; Na 17.25; Cu 4.4; Ag 3.5; Au 3.5.

Be, Mg, Zn, Cd, Hg. The affinity for I increases as we pass from Be to Mg, and thereafter steadily decreases, but remains considerable for all these elements.

Be 10; Mg 10.6; Zn 6.15; Cd 6.1; Hg 3.6.

B, Al, Ga, In, Tl. B has a considerable affinity for I and the affinity increases as we go from B to Al, and then probably decreases as we go towards Tl.

B 3.6; Al 7.5; Ga 6.10; In 6.10; Tl 6.0.

C, Si, Ge, Sn, Pb. C and Si has but feeble affinities for I; the affinity rising steadily as we pass from C to Sn, remaining great at Pb.

C 2.0; Si 3.5; Ge 6.10; Sn 6.10; Pb 5.5.

N, P, As, Sb, Bi. The affinity is very feeble for N, increasing as we pass down the series; becoming great for Sb and Bi.

N 0.1; P 1.0; As 2.4; Sb 3.8; Bi 3.8.

O, S, Se, Te. The affinity for I at O is feeble, and decreases as we pass from O to S. It then again increases as we pass from S to Te but remains feeble here.

O 2.25; S 1.35; Se 1.5; Te 2.0.

F, Cl, Br, I. The affinity is considerable at Cl, decreases thence to Br; and again increases somewhat at I.

F 3.0; Cl 1.8; Br 1.0; I 3.57.

Cross Sections.

Li, Be, B, C, N, O, F. The affinity is great at Li, and steadily decreases as we pass down the series of elements, becoming small at N, then rising again until F.

Li 16; Be 10; B 3.6; C 2; N 0.1; O 2.25; F 3.0.

Na, Mg, Al, Si, P, S, Cl. The affinity is very great at Na, and decreases steadily, becoming very small at S and P, and then increasing somewhat at Cl.

Na 17.25; Mg 10.6; Al 7.5; Si 3.5; P 1.0; S 1.35; Cl 1.8.

Cu, Zn, Ga, Ge, As, Se, Br. The affinity is considerable at Cu, increase somewhat as we pass from Cu to Zn, and then seems to decrease steadily until Br is reached.

Cu 4.4; Zn 6.15; Ga 6.10; Ge 6.10; As 2.8; Se 1.5; Br 1.0.

Ag, Cd, In, Sn, Sb, Te, I. The affinity is considerable for Ag, and rises considerably as we pass from Ag to Cd; it then sinks steadily up to Te, but is still considerable at I.

Ag 3.5; Cd 6.1; In 6.0; Sn 6.10; Sb 3.8; Te 2.0; I 3.57.

Au, Hg, Tl, Pb, Bi. The affinity is very small at Au, rises greatly as we pass from Au to Hg, probably attaining a maximum at Tl. At Pb the affinity is strong, and sinks somewhat as we pass from Pb to Bi.

Au 0.5; Hg 3.6; Tl 6.0; Pb 5.5; Bi 3.8.

Gold.

Longitudinal Sections.

H, Li, Na, Cu, Ag, Au. Affinity for all is very feeble.

H 0.1; Li 0.1; Na 0.1; Cu 0.1; Ag 0.1; Au 0.1.

Be, Mg, Zn, Cd, Hg. The affinity for Au is very feeble for all these elements.

Be 0.1; Mg 0.1; Zn 0.1; Cd 0.1; Hg 0.1.

B, Al, Ga, In, Tl. All have but a feeble affinity for Au.

B 0.1; Al 0.1; Ga 0.1; In 0.1; Tl 0.1.

C, Si, Ge, Sn, Pb. Carbon has but a very slight affinity for Au. Si has probably still less. The others have still smaller affinities.

C 0.1; Si 0.1; Ge 0.1; Sn 0.1; Pb 0.1.

N, P, As, Sb, Bi. N has very little affinity for Au; P a considerably greater affinity. The attraction for Au seems to increase as we go from N to P, and then somewhat slowly decreases.

N 0.1; P 0.3; As 0.2; Sb 0.15; Bi 0.14.

O, S, Se, Te. The attraction for Au is feeble for O, and decreases as we pass from O to Te. All however have a perceptible affinity.

O 0.5; S 0.4; Se 0.3; Te 0.3.

F, Cl, Br, I. The affinity for Au seems very feeble for F and increases considerably as we pass from F to Cl; it then decreases slowly, but remains for I greater than for F.

F 0.3; Cl 2.0; Br 0.8; I 0.4.

Cross Sections.

Li, Be, B, C, N, O, F. The affinity for Au is very small for Li and seems to steadily increase until O is reached. It then decreases somewhat as we pass from O to F. The affinity is feeble throughout the series.

Li 0.1; Be 0.1; B 0.1; C 0.1; N 0.1; O 0.5; F 0.3.

Na, Mg, Al, Si, P, S, Cl. The affinity for Au is very feeble at Na and seems to continually increase as we pass from Na to P, decreases somewhat from P to S and then increases from S to Cl.

Na 0.1; Mg 0.1; Al 0.1; S 0.4; P 0.3; S 0.4; Cl 2.0.

Cu, Zn, Ga, Ge, As, Se, Br. The affinity for Au is exceedingly small both for Cu and Zn. It is feeble but perceptible for Se, and still more perceptible for Br.

Cu 0.1; Zn 0.1; Ga 0.1; Ge 0.1; As 0.2; Se 0.3; Br 0.8.

Ag, Cd, In, Sn, Sb, Te, I. The affinity for Au is very feeble all through the series. It seems to increase as we go from Ag to Cd; and then sinks until Sn is reached. It then rises until I is reached, but even here the affinity is very feeble.

Ag 0.1; Cd 0.1; In 0.1; Sn 0.1; Sb 0.1; Te 0.3; I 0.4;

Au, Hg, Tl, Pb, Bi. The affinity for Au is very feeble throughout the series.

Au 0.1; Hg 0.1; Tl 0.1; Pb 0.1; Bi 0.1.

Mercury.

Longitudinal Sections.

H, Li, Na, Cu, Ag, Au. The affinity of H for Hg is very small. The affinity attains a considerable value at Li; rises some-

what as we pass from Li to Na, then falls as we proceed towards Au.

H 0.1; Li 4.8; Na 5.0; Cu 1.0; Ag 1.0; Au 1.0.

Be, Mg, Zn, Cd, Hg. All have but a very feeble affinity for Hg.

Be 1; Mg 1; Zn 0.3; Cd 0.3; Hg 0.3.

B, Al, Ga, In, Tl. All have very feeble affinities for Hg.

B 0.5; Al 0.3; Ga 0.3; In 0.3; Tl 0.3.

C, Si, Ge, Sn, Pb. C has a very feeble affinity for Hg, and Si probably still less. The affinity seems to decrease as we pass from C towards Pb.

C 0.5; Si 0.3; Ge 0.3; Sn 0.3; Pb 0.3.

N, P, As, Sb, Bi. The attraction for Hg is very small at N, increase as we pass from N to As, then probably decreases somewhat.

N 0.1; P 0.3; As 0.5; Sb 0.2; Bi 0.2.

O, S, Se, Te. O has a very perceptible, but feeble affinity for Hg, and the affinity decreases as we pass from O to S. It again rises as we pass from S to Se; and then again falls as we pass from Se to Te.

O 3.0; S 1.4; Se 2.5; Te 2.0.

F, Cl, Br, I. F has but a feeble affinity; the affinity increases considerably as we pass from F to Cl, it then decreases steadily until I is reached.

F 3; Cl 8.0; Br 6.1; I 3.6.

Cross Sections.

Li, Be, B, C, N, O, F. The attraction of Hg for Li is very considerable, the attraction sinks rapidly as we pass from Li to Be, and remains small until N is reached. It then rises as we pass from N to O and attains a maximum at O, decreasing again as we pass from O to F.

Li 4.8; Be 1.0; B 0.5; C 0.5; N 0.1; O 3.1; F 3.0.

Na, Mg, Al, Si, P, S, Cl. The attraction is great for Na and falls to a small value as we pass from Na to Mg; it remains

small until Si is reached, and then rises steadily to Cl, when the attraction attains its greatest value.

Na 5; Mg 1.0; Al 0.3; Si 0.3; P 0.3; S 1.4; Cl 8.0.

Cu, Zn, Ga, Ge, As, Se, Br. For the first four elements the attraction for Hg is small, at As it becomes appreciable and rises rapidly until Br is reached, where it attains its greatest value.

Cu 1.0; Zn 0.3; Ga 0.3; Ge 0.3; As 0.5; Se 2.5; Br 6.1.

Ag, Cd, In, Sn, Sb, Te, I. The first four elements have all an exceedingly small affinity for Hg. The attraction becomes considerable at Te and reaches its greatest value at I.

Ag 1.0; Cd 0.3; In 0.3; Sn 0.3; Sb 0.2; Te 2.0; I 3.6.

Au, Hg, Tl, Pb, Bi. The attraction for all these elements is small, but seems greatest in the case of gold.

Au 1.0; Hg 0.3; Tl 0.3; Pb 0.3; Bi 0.2.

Thallium.

Longitudinal Sections.

H, Li, Na, Cu, Ag, Au. The affinity of all for Tl is very feeble.

H 0.1; Li 0.3; Na 0.3; Cu 0.3; Ag 0.3; Au 0.3.

Be, Mg, Zn, Cd, Hg. All have but a very feeble affinity for Tl.

Be 0.3; Mg 0.3; Zn 0.3; Cd 0.3; Hg 0.3.

B, Al, Ga, In, Tl. Nothing is known of the affinities of B, Al, Ga, In for Tl; Tl atoms seem to have a tendency to associate together. All have probably but a feeble affinity.

C, Si, Ge, Sn, Pb. Nothing is known of the affinities which C, Si, Ge exert on Tl. But they are probably very feeble; Sn and Pb have but very feeble affinities.

N, P, As, Sb, Bi. No nitride of Tl is known, and it is probably very unstable. P has but a feeble affinity, As an appreciable affinity. The affinity seems to rise as we pass from N to As and then falls to a very small value again at Sb and Bi.

N 0.3; P 0.5; As 0.8; Sb 0.3; Bi 0.3.

O, S, Se, Te. The affinity for Tl is great at O and falls as we pass from O to Te.

O 5.3; S 2.7; Se 2.21; Te 1.60.

F, Cl, Br, I. All these elements have a very great affinity for Tl, the affinity seems to be greatest at F and steadily falls until I is reached.

F 15; Cl 12.3; Br 10.3; I 8.

Cross Sections.

Li, Be, B, C, N, O, F. The attractions which Li, Be, B, C, N exert on Tl are unknown but probably very feeble. O exerts a considerable attraction and the attraction increases considerably as we pass from O to F.

Li ?; Be ?; B ?; C ?; N ?; O 5.3; F 15.0.

Na, Mg, Al, Si, P, S, Cl. Compounds of Tl with Na, Mg, Al and Si are completely uninvestigated, and also the forces which Tl exerts on these elements is completely unknown, but in all probability are very feeble. P possesses a very feeble attraction for Tl, S a considerable, and Cl a very great attraction. The affinity rises rapidly as we pass from P to Cl.

Na ?; Mg ?; Al ?; Si ?; P 0.5; S 2.7; Cl 12.3.

Cu, Zn, Ga, Ge, As, Se, Br. The affinities which Cu, Zn, Ga, Ge possess for Tl are unknown, since no compounds of these elements with Tl have as yet been investigated. The affinities are in all probability very feeble. As has a small but very appreciable affinity for Tl; Se a considerable affinity, and Br a very great affinity. The affinity rises rapidly as we pass from As to Br.

Cu ?; Zn ?; Ga ?; Ge ?; As 0.8; Se 2.21; Br 10.3.

Ag, Cd, In, Sn, Sb, Te, I. Ag, Cd, Sn, Sb all possess a very feeble affinity for Tl. Te possesses a very considerable affinity; and I a still greater affinity. The affinity rises steadily from Sb to I.

Ag 0.3; Cd 0.3; In 0.3; Sn 0.3; Sb 0.3; Te 1.6; I 8.0.

Au, Hg, Tl, Pb, Bi. All have a very feeble affinity for Tl.

Au 0.3; Hg 0.3; Tl 0.6; Pb 0.3; Bi 0.3.

L e a d.

Longitudinal Sections.

H, Li, Na, Cu, Ag, Au. For all is the affinity for Pb feeble, rising as we pass from H to Li, then sinking up to Ag, then probably rising somewhat at Au.

H 0.1; Li 1.4; Na 1.5; Cu 0.5; Ag 0.5; Au 1.0.

Be, Mg, Zn, Cd, Hg. All these have but a very feeble affinity for Pb; the affinity decreasing as we pass from Be to Hg.

Be 1; Mg 0.8; Zn 0.7; Cd 0.5; Hg 0.4.

B, Al, Ga, In, Tl. All these bodies have a very feeble affinity for Pb.

B 0.5; Al 0.5; Ga 0.5; In 0.5; Tl 0.5.

C, Si, Ge, Sn, Pb. All the substances have but a feeble affinity for Pb.

C 0.2; Si 0.5; Ge 0.5; Sn 0.5; Pb 0.5.

N, P, As, Sb, Bi. The affinity for lead for all these elements is very feeble, rising from N to As and then sinking up to Bi.

O, S, Se, Te. O has a very considerable affinity for Tl, and the affinity steadily decreases until Te is reached.

O 6.25; S 3; Se 2; Te 1.5.

F, Cl, Br, I. For all these elements the affinity for Pb is very great. The affinity being greatest at F and sinking thence to I.

F 14; Cl 2; Br 9; I 5.5.

Cross Sections.

Li, Be, B, C, N, O, F. Up to N the affinity for Pb is feeble; at O it becomes great, and rises thence up to F.

Li 1.4; Be 1.0; B 0.5; C 0.2; N 0.2; O 6.25; F 14.0.

Na, Mg, Al, Si, P, S, Cl. N has a small but appreciable affinity for Pb, the affinity decreasing as we pass from Na to Mg, remaining very small until P is reached. It then rises, becoming considerable for S and great for Cl.

Na 1.5; Mg 0.8; Al 0.5; Si 0.5; P 0.7; S 3.0; Cl 11.

Cu, Zn, Ga, Ge, As, Se, Br. The first four elements have but a feeble affinity for Pb, the affinity then increases, attaining its greatest value at Br.

Cu 0.5; Zn 0.7; Ga 0.5; Ge 0.5; As 1.0; Se 2.0; Br 9.0.

Ag, Cd, In, Sn, Sb, Te, I. Up to Sb the affinity is very small, it rises to a considerable value at Te; and becomes great at I.

Ag 0.5; Cd 0.5; In 0.5; Sn 0.5; Sb 0.5; Te 1.5; I 5.5.

Au, Hg, Tl, Pb, Bi. Au has a small but appreciable affinity for Pb. The affinity falls as we pass from Au downwards.

Au 1.0; Hg 0.4; Tl 0.5; Pb 0.5; Bi 0.5.

B i s m u t h.

Longitudinal Sections.

H, Li, Na, Cu, Ag, Au. H has a very feeble affinity for Bi; Li and Na considerable affinities; Cu, Ag, Au small affinities. The affinity rises rapidly as we pass from H to Li, sinks as we pass from Na to Cu, and remains small, but appreciable, until Au is reached.

H 0.1; Li 2.5; Na 2.5; Cu 0.5; Ag 0.5; Au 0.5.

Be, Mg, Zn, Cd, Hg. Be and Mg have probably very feeble affinities for Bi, and the others still smaller affinities.

Be 0.8; Mg 0.5; Zn 0.1; Cd 0.5; Hg 0.2.

B, Al, Ga, In, Tl. All have a very feeble affinity for Bi.

B 0.5; Al 0.5; Ga 0.5; In 0.5; Tl 0.3.

C, Si, Ge, Sn, Pb. Affinity for Bi is very feeble for all.

C 0.5; Si 0.5; Ge 0.5; Sn 0.5; Pb 0.3.

N, P, As, Sb, Bi. All have but a very feeble affinity for Bi.

N 0.3; P 0.6; As 0.7; Sb 0.5; Bi 0.5.

O, S, Se, Te. Bi has a considerable affinity for O, and the affinity steadily decreases as we pass towards Te; Te has but a feeble affinity for Bi.

O 5.8; S 3; Se 2; Te 1.5.

F, Cl, Br, I. The affinity for Bi is great for all these elements decreasing from F to I.

F 9; Cl 7.6; Br 6.25; I 4.0.

Cross Sections.

Li, Be, B, C, N, O, F. Li has a very appreciable affinity for Bi, the affinity decreasing as we pass from Li to N, where it is very small; it then increases rapidly becoming great at O, and attaining its greatest value at F.

Li 2.5; Be 0.8; B 0.5; C 0.5; N 0.3; O 5.0; F 9.8.

Na, Mg, Al, Si, P, S, Cl. The affinity of Na for Bi is very considerable, becoming small as we pass from Na to Mg, and remains very small until P is reached. As we pass from P to S, the affinity increase and becomes great at Cl.

Na 2.5; Mg 0.5; Al 0.5; Si 0.5; P 0.6; S 3.0; Cl 7.3.

Cu, Zn, Ga, Ge, As, Se, Br. The affinity for Bi is very small for all these elements. It remains very small until As is reached. At Se it becomes appreciable, at Br great.

Cu 0.5; Zn 0.1; Ga 0.5; Ge 0.5; As 0.7; Se 2.0; Br 5.3.

Ag, Cd, In, Sn, Sb, Te, I. The affinity for Bi for all these elements is very small, becoming appreciable first for Te, and considerable for I.

Ag 0.5; Cd 0.5; In 0.5; Sn 0.5; Sb 0.5; Te 1.5; I 4.2.

Au, Hg, Tl, Pb, Bi. The affinity for all these substances for Bi is exceedingly feeble.

Au 0.5; Hg 0.2; Tl 0.3; Pb 0.3; Bi 0.5.



Chapter V.

The connection between the form of the affinity surfaces of elements and their chemical properties; and on the Wave Law of affinity in the Periodic System.

The different chemical attractions which the various elements exert on each other are the direct underlying cause of all the changing phenomena of Chemistry.

The study of these forces is therefore a matter of great importance. An atom has in general a greater chemical attraction for some elements than for others.

We find, for example, that while F has a great affinity for H, it has no affinity for O; that while N readily unites with B and P to form compounds characterised by their great stability, it refuses to combine at all with flourine and sodium.

We propose in this chapter to make clear the law underlying this phenomenon.

If the chemical properties of elements really depend in the way we have imagined upon their affinities, and that consequently the shape of their affinity surfaces accurately reflect the chemical characteristics of an element, then the fact that different elements possess different properties must reveal itself geometrically in the difference in the shape of their affinity surfaces.

The theory of the preceeding chapters (chapter 2) shows that chemically similar elements must possess characteristic surfaces of a similar shape, and chemically unlike elements of an unlike shape. We propose now to investigate more closely the exact nature of the dependence of the chemical properties of elements upon the shape of their affinity surfaces.

The best method to do this is to systematically study the normal affinity surfaces of a large number of elements of the periodic system such as is given in the last chapter.

An inspection of these surfaces reveals the following facts:

The affinity surfaces of chemically similar elements are of a similar shape, and those of chemically unlike elements of a dissimilar shape, as is demanded by the theory of chapter II.

The best way to demonstrate this is to contrast the affinity surfaces for some sets of typically similar elements such as Li, Na and K; B and Si; F, Cl, Br and I; which are given in the last chapter and exhibited on the large plate at the end of the book.

In fact in the case of all chemically similar elements, there is a very close resemblance in the shape of the affinity surfaces. And a detailed study of them will show that the more alike are the elements chemically, the closer, the resemblance between their affinity surfaces and that conversely the more unlike are the elements the more unlike are their affinity surfaces.

For example the affinity surfaces of the pairs of elements Cl and Br; B and Si; Na and K; resemble each other very closely in shape, and these are also the pairs of elements which approach each other very closely in properties.

F however differs appreciably in properties from Cl and Br, and seems to be approaching O in properties*) and we find also that the affinity surface of fluorine differs appreciable from that of Cl and Br, and seems to approximate in shape to the affinity surface of oxygen. Similarly the chemical properties of iodine, and also the shape of its affinity surface, differ appreciably from those of Cl and Br, and still more from that of F.

In fact the increasing dissimilarity of the elements, as we pass from F to I, is exactly depicted by an increasing difference

* Moissan. Bull. Soc. Chim. (1891) (3) V, 880.

Martin. Chem News. (1904). 89. 49.

See also p. 69.

in the form of their affinity surfaces, the end points of the series of halogens, viz F and I, presenting widely dissimilar properties and widely dissimilar affinity surfaces.

The same is the case with the series of elements Li, Na, K, — the affinity surface of Li and also its properties differing appreciably from those of Na and K, and tending to approach those of Mg or Be.

The affinity surfaces of elements do, therefore, really picture accurately the chemical properties of elements, the condition of chemical similarity being that the affinities which the elements exert must be proportional.

The form of the affinity surface of a metal is diametrically opposite to that of a non-metal.

The best method of studying this question, and thus of determining what is characteristic of the metallic and of the non-metallic condition, is to watch the gradual change in the form of the affinity surface of a series of elements, which pass gradually from a non-metallic to a metallic condition and vice versa.

For example (see plate at end of book) those of the series of elements Li, Be, B, C, N, O, F, where starting with a pronounced metal, Li, we pass with increase of atomic weight to a pronounced non-metal F.

Or again, those of the series N, P, As, Sb, Bi and C, Si, Ge, Sn, Pb, which furnish examples of series of elements which start with non-metals and pass with increase of atomic weight into metals. In every case we find that the passage of the elements from non-metals into metals, is attended by a transformation of the shape of the affinity surface from the form of an irregular wave surface which has its crest over the early groups of the periodic system (eg. the alkali or alkali earth metals) to the form of an irregular wave surface which has its crest over elements of the later groups of the periodic system (such as the oxygen or halogen elements).

And that elements of intermediate properties possess surfaces of shapes intermediate between those of pronounced metals and pronounced non-metals.

When we contrast the characteristic surfaces of Li and F, Na and Cl, K and Br — that is, the elements at the extremities of each cycle of the periodic system — a very remarkable fact appears. We find that the surfaces of Li, Na, K are of almost exactly the same shape as the corresponding surfaces of F, Cl, Br, except that they bear to them the same relationship that the image of an object in a mirror bears to the object — the surfaces of Li, Na, K being "right-handed" mirror images of the "left-handed" surfaces of F, Cl and Br. For example by viewing the surface for chlorine in a mirror we might easily imagine we were viewing the surface of sodium, as the reader may easily verify by holding a mirror before the affinity surface of chlorine, and comparing the reflected image with the affinity surface of sodium. The resemblance goes into detail. For example, Li differs appreciably in properties from Na and K, and tends to resemble somewhat the elements of the next group.

So also the element at the other extreme of the cycle of elements Li, Be, B, C, N, O, F, namely fluorine, differs appreciably in properties from Cl and Br, and tends to resemble somewhat the elements of the next group, viz. O.*)

And this fact is reflected in the increased resemblance, on the one hand, of the affinity surface of Li to that of Mg, and its difference from those of Na and K; and on the other hand, in the increased resemblance of the affinity surface of F to that of O, and its difference from those of Cl and Br.

This seems very remarkable, and indicates that Li, Na, K bear precisely the same relationship to the neighbouring elements of group I and II, as do F, Cl, Br to the elements of group VII and VI.

We give part of the Periodic System to illustrate this remark:

Groups	I	II	III	IV	V	VI	VII
	Li	Be	B	C	N	O	F
	↑						↑
	Na	Mg	Al	Si	P	S	Cl
	↑						↑
	K						Br

*) See p. 181.

As the arrows, show, it seems as if Li, on the one hand, tends to pass out of group I into group II, and that F similarly tends to pass out of group VII into group VI.

The same seems true of the heavier elements of the series.

For example, Ag and Au of group I show analogies to Hg of group II. Ba and Tl of groups II and III show analogies to Pb of group IV.

The chemical inactivity of nitrogen is to a great extent only an apparent effect.

A study of the affinity surface of nitrogen shows that the point of maximum chemical affinity lies over boron.

When we contrast this surface with the affinity surfaces of K and Cl, it becomes manifest that while K expends its energies upon elements belonging to the later groups of the Periodic System (viz. O, S, Se, and F, Cl, Br, I) but has little affinity for elements of the earlier groups (such as the alkali metals and alkali earth metals) and that while chlorine expends its energies principally upon the elements of the early groups of the Periodic System (such as the alkali metals and alkaline earth metals), but has little affinity for the elements of later groups (such as the halogens and oxygen group of elements) that, in contradistinction to these, nitrogen expends its energies on elements of intermediate groups — principally on those of groups III, IV and V — but has little affinity for those of earlier or later groups (such as the alkali elements and the halogens).

Its combinations with boron, silicon and phosphorous are quite remarkable by reason of their great stability.

For example, the phosphide P_3N_5 must be heated in oxygen gas to a temperature above that at which hard glass melts, before the oxygen begins to act on it!

The current belief that nitrogen is an element characterised by its chemical inertness, and by the feebleness of its chemical affinities is therefore hardly correct.

Nitrogen possesses chemical affinities of a strength almost comparable with those of chlorine or potassium, only it differs from these elements as regards the elements it exerts them on.

The chemical activity of oxygen and potassium is more apparent to us than is the chemical activity of nitrogen, principally because they happen to possess very powerful affinities for some of the most prominent and abundant elements by which we are surrounded, whereas nitrogen possesses but feeble affinities for such elements but strong affinities for elements which happen not to be prominent or abundant in the laboratory. Nitrogen is doubly unfortunate in this respect, for the elements for which it possesses the strongest affinity are elements which occur in the middle of cycles of the Periodic System, and so are precisely those which happen to possess the power of self combination most strongly developed. This circumstance lowers the apparent stability of the compounds they produce with nitrogen in the way explained on pp. 187—189.

It should be remembered that oxygen itself has but a feeble affinity for N; F, Cl, Br, I &c.; and were these the only common or prominent elements, we would consider O to be quite as inactive an element chemically as N appears to us under ordinary circumstances. The compounds of O with Cl, for example, are characterised by their explosive properties, just as are so many nitrogen compounds.

The affinity surface of hydrogen shows that it belongs to the alkali metall group and not to the chlorine group of elements.

Within recent years a discussion has arisen as to whether hydrogen should be placed at the head of the alkali group or at the head of the halogen group of elements.*)

Some three years ago (Chem. News [1901], 84, 154) I published a paper in which this point was discussed and then came to the conclusion that H could not belong to the halogen elements. The discussion as to whether a particular element belongs to this or to that group of the Periodic System is perhaps only a question of transitory importance. For when we know the cause of the periodic law we will ease to trouble about the particular position of an element in the Periodic System, just as

*) For example see Orme Masson. Chem. News. 73. 283.

Crookes. Proc. Roy. Soc. (1898). 405.

Ramsay. Proc. Roy. Soc. Jan. 8th 1900.

when the valency theory revealed the cause of the different types of combination, men ceased to dispute as to whether a compound belonged to this or to that type of combination.

However this may be, the results obtained in this research throw fresh light on the relation which H bears to the other elements, and seems to conclusively refute the view that hydrogen should be associated with the halogens rather than with the alkalis. In the previous chapter we gave in a table a survey of the stability of the hydrides, so far as they are known, of the elements of the primary system A. From this datum is constructed the affinity surface of hydrogen, given in the plate at the end of the book.

A study of this shows that so far as the chemical affinities of H are concerned, it belongs entirely to the alkali group, having affinities of a diametrically opposite nature to chlorine. In fact, in contrasting the affinity surfaces of the alkalis and the halogens with that of H, it becomes at once apparent that the affinity surface of hydrogen possesses a shape similar to that of the affinity surface of Na or K (and still more closely to that of Mg) and is quite different in almost every respect to those of Cl or Br.

We conclude from this, that the inner structure or constitution of the hydrogen atom (which presumably determines its affinities) is probably akin to the inner structure or constitution of the sodium or potassium atom and is opposite in nature to that of the chlorine or bromine atom; so that hydrogen should be classed with the alkalies rather than with the halogens.

The point of maximum affinity shifts from F to Li as we pass from Li to F.

If we arrange in order the affinity surfaces of the elements of the first series of the Periodic System (viz. Li, Be, B, C, N, O, F), a remarkable fact becomes apparent.

The affinity surfaces of the successive elements assume the appearance of successive positions of an advancing wave, whose crest appears on the extreme right hand side of the diagram in the case of Li and then sweeps from right to left as we pass

from Li towards F, until at F the crest is on the extreme left hand side.

For example, in the case of Li the point of maximum affinity (that is, the highest point or crest of its affinity surface) is over F or Cl. Passing from Li to B the point of maximum affinity shifts towards N — BN being a body of very great stability. With C it lies over C itself — and hence the remarkable power of self combination which C possesses; its great involatility, and as diamond, its marvellous hardness, are all evidences of the great attractive force with which the C atoms cohere together.

Passing from C to N the point of maximum affinity passes from C to B, BN being probably the most stable nitride which N produces. Now passing from N to O, the point of maximum affinity shifts from B to Be or Li — both BeO and Li_2O — being bodies of very great stability.

Finally passing from O to F, the point of maximum affinity shift up to Li — the ratio of the attraction which Li exerts on F to that which Be exerts on F, being considerably greater than the ratio of the attractions which Li exerts on O, to that which Be exerts on O.

An inspection of the affinity surfaces of these elements will at once make this fact apparent.

The same phenomenon appears with the elements of the third (Na, Mg, Al, Si, P, S, Cl, Ar) cycle, and later cycles of the periodic law, only in most cases the wave form seems to pass more or less discontinuously from right to left, and there often seems to be a depression at the elements of the fourth group — probably an apparent effect due to the abnormally developed power of self combination possessed by these elements. For example, when we compare the heats of formation of the two oxides of carbon, we have according to Thomsen the following numbers:

$$\begin{aligned}(\text{C}, \text{O}) &= 29,000 \\ (\text{CO}, \text{O}) &= 67,960\end{aligned}$$

So that the addition of the second atom of oxygen to the carbon atom is attended with the liberation of a far greater quantity of visible heat than the addition of the first atom. This is a remarkable result quite at variance with the usual rule (see

appendix A) which holds in chemistry, and the explanation is probably that the small quantity of heat evolved in the formation of CO is due to the fact that before an oxygen atom can combine at all with a carbon atom it has to separate it from its combination with other carbon atoms. The carbon atoms attract each other very strongly indeed, as is shown not only by their great power of self-combination, but also by the great hardness and involatility of certain forms of carbon. Consequently this initial separation of the carbon atoms absorb a very large quantity of heat and this lowers the apparent heat of formation of CO much below its real value.

In gaseous CO, however, the carbon atoms are already separated and so no further great quantity of heat is absorbed before the additional O can be added on to form CO₂. It is very probable, therefore, that the apparent heats of formation and stability of the oxides and indeed of all other compounds of carbon are very much below their real values on account of the exceptionally large quantities of heat absorbed in separating the carbon atoms from each other. This is probably the reason why the heat of formation of CH₄ is less than the heat of formation of SiH₄, although CH₄ is a much more stable body than SiH₄. (See p. 47).

Silicon is the element next to carbon which possesses to the greatest extent the power of self-combination.

The apparent heat of formation of its oxide is also, therefore, probably much less than its true value. In the case of certain monatomic atoms, such as sodium, mercury &c., and of elements in which the power of self-combination is but slightly developed, the apparent heats of formation probably correspond fairly closely with the real heats of formation.

We should therefore expect that when we come to compare the thermal data and stability of the compounds of the various elements we will find that there is an apparent general depression very much below their true values as we approach such elements as carbon and silicon which lie in the middle of a cycle of elements of the Periodic System, where the power of self-combination is abnormally developed.

Whereas there would be nearly correct values for such elements as Na, Hg &c. which lie on the extreme borders of the cycle where the power of self-combination is but feebly developed.

A glance at the relative magnitudes of the affinity surfaces of the successive elements exhibited in the large plate at the end of the book will show that this is actually the case.

The chemical affinities of heavy elements are in general much feebler than those of lighter elements.

This at once appears by surveying the affinity surfaces of the corresponding elements of the successive cycles of the periodic system. It will be found that the affinity surfaces seem to shrink up as we pass from elements of the early series to those of later series.

A comparison of the affinity surfaces of Li, Be, B, C, N, O, F, with those of Ag, Cd, In, Sn, Sb, Te, I, or still better those of Au, Hg, Tl, Pb, Bi will show the general truth of this remark. Heavy elements thus tend to become chemically inert. It will be noticed that hydrogen (of the first series) also possesses very feeble affinities.

In the course of these investigations it has often struck me as remarkable that if the atoms of an element in any one cycle of the Periodic System attracts atoms of other kinds very strongly they possess a correspondingly weak attraction for atoms of other kinds. Every atom of a cycle in the Periodic System seems, in fact, to possess what may be called a "Conservation of attraction", If this is really true, the Volumes enclosed by the wave surfaces of all the successive elements of any one cycle of the Periodic System would be the same — the volumes altering in steps, as it were, as we pass from one cycle to another of the Periodic System, but remaining constant throughout any one cycle of the elements.

The growth in volume of the affinity surfaces as we pass from the elements of the first series (represented by hydrogen) to the elements of the second or third series, and the subsequent steady decrease in volume as we pass onwards to elements of still heavier series must regulated by some law, simple or complex, and the law just mentioned seems to be a probable one.

as will be seen by glancing at the relative magnitudes of the affinity surfaces of the elements of the successive cycles of the Periodic System set forth in the large plate at the end of the book.

However the data is not sufficient to confirm this suspicion, and what is still worse, the data is masked by the effects of the power of self-combination of the atoms, referred to on pages 188—189. (See also pp. 46—47, 136—137 &c.).

The subject is worthy of further research since the law if found correct would obviously have an important bearing on the problem of the origin of the elements. For further remarks on this point the reader is referred to the preface.

It is curious to note that those elements which possess the strongest affinities seem to be in general the most abundant in nature; and those which possess weak affinities in general un-abundant.

Are elements with strong affinities more stable than elements with weak affinities?*)

The wave law of affinity in the Periodic System.

The periodic law shows that there is a connection between the atomic weights of elements and their properties, the connection being of such a nature that as the atomic weight increases the properties gradually alter and then suddenly (after passing through an element of zero affinity such as Ne or Ar) at the end of a cycle return to nearly but not quite their original values. So that if the elements are arranged in the order of their atomic weights — from H, the lightest as unity, to uranium, the heaviest, as 240 — the series does not exhibit one continuous progressive modification in the physical and chemical characteristics of its several terms, but breaks up into a number of sections, in each of which the several terms present analogies with corresponding terms of other series.

Thus the whole series does not run **)

a, b, c, d, e, f, g, h, i, j, k &c.

but

a, b, c, d, A, B, C, D, α , β , γ , δ , &c.

*) Chem. News. 1904). 89. 47, 118.

**) The illustration is from Huxley, Method and Results. p. 76-77.

Now the theory developed in the preceding pages, shows that the chemical properties of elements depends upon their attractive forces.

Hence if our theory is correct, there must be a connection between the atomic weights of elements and their attractive forces, the connection being of such a nature that as the atomic weight gradually increases the attractive forces gradually alter, and then suddenly return to nearly but not quite their original values — going through, as it were, cycles.

It is clear, therefore, that there must be a connection between the shape of the affinity surfaces of elements and their atomic weights — the shape gradually altering as the atomic weight alters, and then returning suddenly at the end of a cycle, to nearly but not quite its original shape.

And this is actually the case. We find that if we arrange the elements in the order of their atomic weights, the affinity surfaces of the successive elements assume the appearance of successive positions of an advancing wave, whose crest coming into the field of view on the extreme right hand side of the diagram, gradually sweeps from right to left, altering its form continually as it passes down the field, then passing out of view on the left. This is followed by the appearance of a new crest, on the extreme right hand side of the diagram, of nearly, but not quite the original form, which then in its turn sweeps down the field of view and disappears, and so on, the one crest following the other like the successive waves on the sea shore — the appearance of each new wave crest heralding the appearance of a new cycle of elements.

At the moment where the one crest passes out of the field of view on the left, and a second has not yet made its appearance on the right, we get an element of zero affinity, belonging to the argon family.

As regards the elements of the primary system A this is always the case. In the case of the elements of the primary system B this is not the case, for before the one crest passes out of the field of view another crest has already begun to sweep down the field, and hence elements of zero affinity do not occur

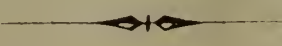
at all, but elements of intermediate properties such as Fe, Co, Ni; Ru, Rh, Pd; Os, Ir, Pt.

There can, I think, be little doubt that a great many of the irregularities shown by the affinity surfaces of the elements in the large plate at the end of the book, are due to defective data, or to errors introduced by the secondary causes discussed on pp. 46—47, 136—137, 188—189, to which pages the reader is referred for a fuller discussion. This especially applies to the surfaces of carbon, silicon, boron and nitrogen, where these secondary causes attain their greatest value. The affinity surfaces here described are those which correspond to the affinities the elements exert at normal temperatures. The form of the affinity surfaces varies in a definite way as we increase the temperature whereat the elements are viewed. We will discuss this point further in Chapter VII.

Mathematical expression of the periodic law.

The gradual change in the form of the affinity surfaces of the successive elements is, of course, mathematically expressible by alterations in the forms of their equations.

And the law of variations, whereby the affinity surfaces of the successive elements are derived successively one from the other, is the quantitative mathematical expression of the periodic law. Since we can regard the affinity surfaces of the elements as successive forms of a single wave surface which is gradually altering its type, it is theoretically possible to express the whole of the periodic law by a complicated periodic function of x , y , z and from this expression could be deduced the characteristic surface of any known element included in the scheme of the periodic law, and thus all those properties of any known element which depend upon the chemical forces which it exerts. It is thus theoretically possible to comprise in a single mathematical expression consisting of three variables only, the whole range of facts relating to all the elements and their properties — that is to say, practically the whole of inorganic chemistry. A very simple solution of this problem has already been given on p. 35.



Chapter VI.

Theory of the alteration in the properties of elements and compounds.

The affinities of elements are not constant.

In chapter 1 it was shown that the properties of an element or compound depend upon its affinities $f_1, f_2, f_3, f_4 \dots \dots f_n$. and that to each element may be ascribed a characteristic surface whose form depends solely upon the magnitude of these affinities; and whose equation expresses the properties of the element in the same way that the equation of an algebraical curve expresses the geometrical properties of the curve. Hence we can represent the properties of an element as a definite algebraical function of $f_1, f_2, f_3, f_4, \dots \dots f_n$ i.e

$$P = F(f_1, f_2, f_3 \dots \dots f_n).$$

Now it is possible to alter the attractive forces $f_1, f_2, f_3, f_4 \dots \dots f_n$ which an element exerts on other elements in a great many ways. Of these we may mention the following:

1. By combining it with other atoms.
2. By viewing it at different temperatures.
3. By altering the pressure under which the element is viewed.
4. By changing the medium in which the element is immersed.
5. By altering the electric field in which the element is placed.
6. By altering its valency.

Consequently if we subject the element to any of these influences we alter the shape of its characteristic surface which depends upon the magnitude of these attractive forces.

Suppose now we apply any influence whatever to the element which causes it to alter its affinities $f_1, f_2, f_3 \dots f_n$ to $f_1 + k_1 f_1; f_2 + k_2 f_2; f_3 + k_3 f_3 \dots f_n + k_n f_n$.

Then $P_A \equiv F(f_1, f_2, f_3 \dots f_n)$ changes under the influence into $P_B \equiv F(f_1 + k_1 f_1; f_2 + k_2 f_2; f_3 + k_3 f_3 \dots f_n + k_n f_n)$.

And since P_A describes the properties of the element before the influence had began to act on it, P_B must also describe the properties that the element presents after the influence has acted on it.

Hence if $P_A = O$ represents the equation of a surface which describes the properties of the element, $P_B = O$ will represent the equation of the new surface which describes the properties presented by A after the influence has acted on A.

So that the change in properties caused in an element by any external influence can be followed simply by following the change caused by this influence in the shape of the affinity surface of the element.

Hence the transformation of properties brought about by the influence can be represented quantitatively by an analytical expression which expresses the change in the form of the characteristic surface of the element caused by that influence.

This analytical expression can be deduced thus:

The operation represented by $e^{h \frac{d}{dx}}$ when applied to any function of x is equivalent to changing x into $x + h$ throughout that function.

Accordingly

$$e^{h \frac{d}{dx}} \Phi(x, y) = \Phi(x + h, y)$$

similarly,

$$e^{k \frac{d}{dy} + h \frac{d}{dx}} \Phi(x, y) = \Phi(x + h, y + k)$$

Hence the operation of changing

$$P_A = F(f_1, f_2, f_3 \dots f_n)$$

into

$$P_B = F(f_1 + k_1 f_1, f_2 + k_2 f_2, f_3 + k_3 f_3 \dots f_n + k_n f_n)$$

may be shortly denoted by

$$e^{k_1 f_1 \frac{d}{df_1} + k_2 f_2 \frac{d}{df_2} + \dots + k_n f_n \frac{d}{df_n}} P_A = P_B$$

which is the analytical expression for the operation of changing the properties of A by means of some external influence, from those expressed by P_A to those expressed by P_B .

The specific nature of the operation performed on A is quite indifferent.

All that is stated by this nomenclature is that the operation $e^{h_1 \frac{d}{df_1} + h_2 \frac{d}{df_2} + \dots}$ applied to a particular element or compound which is characterised by the forces f_1, f_2, f_3 . Increases f_1 to $f_1 + h_1$, f_2 to $f_2 + h_2$ &c. and thus generates a substance characterised by the different set of forces $f_1 + h_1, f_2 + h_2, f_3 + h_3 \dots f_n + h_n$. The operation may consist in the addition of matter to the atomic species A, causing an increase of atomic weight, which would cause changes in the values of $f_1, f_2, f_3 \dots f_n$. Or the operation may consist of acting on A with the temperature, or of altering the affinities of A by combining it with other atoms.

An important problem now arises.

We have just pointed out that we can alter the affinities and therefore the shapes of the characteristic surfaces of elements in many different ways.

Suppose now we take two atomic species A and B which are chemically unlike, and act on A and B by any or all of the influences previously enumerated; then the characteristic surfaces of A and B would change their shapes. Is it possible to so adjust the influences which act on A to those which act on B as to change the shape of the affinity surface of A so as to make it similar to that of B?

If so we would make the atomic species A and B chemically similar to each other, for the condition of chemical similarity is that A and B should have affinity surfaces of a similar shape.

Analytically we may state the problem thus.

Suppose we have two different atomic species A and B, defined by the equations:

$$P_A = F(f_1, f_2, f_3 \dots f_n) \quad (1)$$

$$P_B = F(f_1', f_2', f_3' \dots f_n') \quad (2)$$

where $f_1, f_2, f_3 \dots f_n$ have the usual meaning.

Suppose further that:

$$\left. \begin{aligned} f_1' &= f_1 + k_1 f_1 \\ f_2' &= f_2 + k_2 f_2 \\ f_3' &= f_3 + k_3 f_3 \\ &\dots \dots \dots \\ f_n' &= f_n + k_n f_n \end{aligned} \right\} \quad (3)$$

where $k_1, k_2, k_3 \dots k_n$ are arbitrary factors so chosen as to fulfil the above relationships.

Then it is required to act on A by means of some external influence so as to change

$$\left. \begin{aligned} f_1 &\text{ into } k \cdot f_1' \\ f_2 &\text{ into } k \cdot f_2' \\ &\dots \dots \dots \\ f_n &\text{ into } k \cdot f_n' \end{aligned} \right\}$$

where k is a constant.

Then in this case the forces $f_1, f_2, f_3 \dots f_n$ which A exerts are made proportional to the forces which B exerts. So that A and B with now become chemically similar.

Therefore any influence or influences which produce the transformation

$$e^{k_1 \cdot f_1 \cdot \frac{d}{df_1} + k_2 \cdot f_2 \cdot \frac{d}{df_2} + \dots \dots \dots k_n \cdot f_n \cdot \frac{d}{df_n}} P_A = P_B$$

will render A and B chemically similar.

Modification of the attractive power of atoms by combining them with other atoms. General theory.

By combining an atom with other atoms we can modify its attractive power to almost any extent, and thus modify its properties to almost any degree.

The compounds of an element may be looked upon as the original element itself modified by the addition of other atoms; for example NH_3 may be looked upon as a nitrogen atom whose attractive power is modified by the addition of three hydrogen atoms, the whole forming a system having quite different properties to the original nitrogen atom.

The system of attractive forces $f_1, f_2, f_3, f_4 \dots f_n$, with which the original nitrogen atom attracted other atoms may be looked upon as still present in the nitrogen atom modified by three atoms of hydrogen — that is to say, in ammonia.

This is clear because ammonia like nitrogen must also in general exert n different attractive forces on the n different elementary forms of matter. But the original forces in the nitrogen atom have become so modified and altered in intensity and relative magnitude by the influences of the H atoms as to pass into an entirely different set of forces $F_1, F_2, F_3, F_4 \dots F_n$ which are in no way comparable with the original system.

If now we think of the compound NH_3 as replaced by these forces (as in chapter I), then the operation of combining the N atom with 3 H atoms is algebraically equivalent to transforming the original system of forces $f_1, f_2, f_3 \dots f_n$ into a new system $F_1, F_2, F_3 \dots F_n$.

And if the original system of forces determine in the way previously indicated a surface which represents the properties of the original nitrogen, then the new system of forces $F_1, F_2, F_3 \dots F_n$ will determine a corresponding surface which represents the properties of NH_3 .

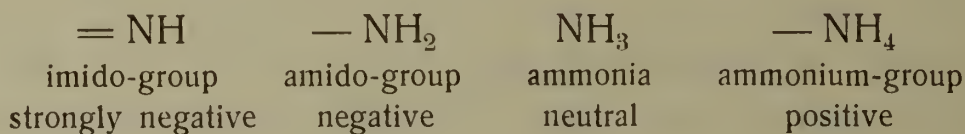
So that geometrically considered, the effect of operating on the original nitrogen atom with three hydrogen atoms is to deflect the original surface into another surface, both of which are perfectly determinate when the magnitudes of $f_1, f_2, f_3 \dots f_n$ and $F_1, F_2, F_3 \dots F_n$ are known.

The operation of producing a compound from an element is thus followed by the change in the surface of the element when converted into the compound.

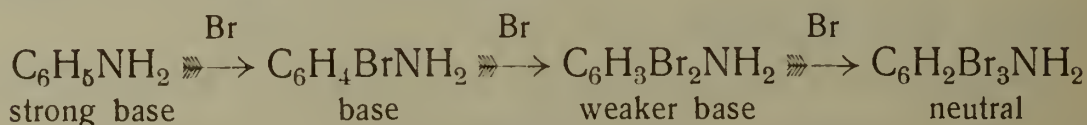
Specific influences exerted by different radicles in altering the attractive forces of elements with which they are made to combine.

This of late years has been widely studied and a full discussion will be found in the works of Ostwald and van't Hoff. For our purpose it is sufficient to remark here that combining an element with positive radicles tends to make it behave like a metal; while combining it with negative radicles tends to make it behave like a non-metal.

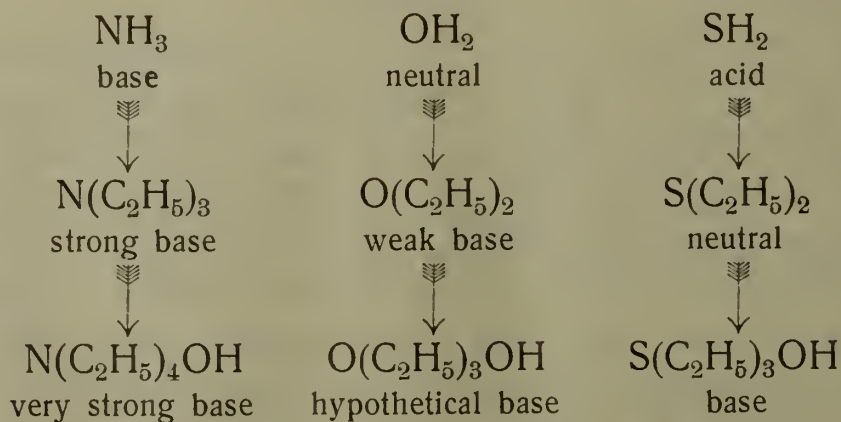
For example, by successively combining an element or radicle with H we make it more positive. Compare:



By successively combining an element with chlorine or bromine we make it more negative:

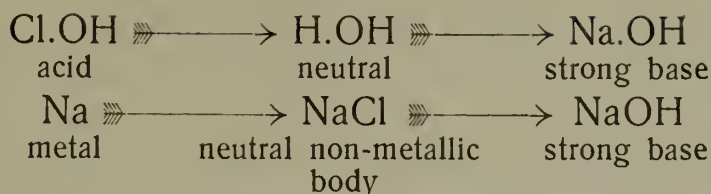


The following scheme show how by acting on different bodies with different radicles we alter their properties:*)



*) See Ber. (1901) 34. 2682.

Notice also :



All these transformations could be represented by means of surfaces in the way previously indicated.

It will thus be seen that we can by combining elements and compounds with different radicles alter their properties to almost any extent and in almost any direction.

Possibility of making dissimilar elements and radicles chemically similar by combining them with other atoms.

We now proceed to illustrate how we can often make elements and compounds which are totally unlike in almost every particular, display the very greatest degree of chemical similarity by suitably modifying their attractive power by combining them with suitable radicles.

Case of nitrogen.

No two elements are more unlike both chemically and physically than nitrogen and sodium. The one is an inert non-metallic gas, having only a very feeble affinity for other atoms and characterised by the unstability and explosive nature of its compounds. The other is a strongly positive and chemically active metal.

By combining N with 4 atoms of H we completely transform its properties. When thus combined the non-metallic nitrogen acts chemically like the metallic Na.

The radicle ammonium NH_4 produces a whole series of salts which correspond in almost every respect to those of the alkali metals — even to the extent of forming a peroxide $(\text{NH}_4)_2\text{O}_2$ which like Na_2O_2 is decomposed by H_2O with the evolution of O and has a strongly alkaline reaction.*)

So great is the resemblance between the ammonium salts and those of Na and K, that they are often described in text-

*) Ber. (1897) 30. 3144—3146.

books of inorganic chemistry along with those of the alkali metals. "Sodium chloride resembles ammonium chloride not only in its outward appearance, but even in crystalline form, in its property of giving precipitates with silver salts, in its solubility in water, and in its evolving hydrochloric acid when heated with sulphuric acid — in a word, a most perfect analogy is to be remarked in a whole series of reaction."*)

By replacing the H by ethyl or methyl, we increase still further the resemblance to K. For example, the compound $\text{Et}_4\text{N.OH}$ is as strong a base as caustic potash, and resembles the latter so closely that it absorbs carbonic acid, is slippery to the touch, cauterizes the skin, drives out ammonia, hydrolyses fats, and gives salts with acids with the evolution of heat.

According to the preceding theory, the reason of the resemblance of these ammonium radicles to the Na atom is simply that these ammonium radicles are arrangement of atoms so combined together as to exert on other atoms forces of the same intensity (or of a proportional intensity) as the elementary Na atoms which they play the part of.

By combining nitrogen with nitrogen we can modify its properties in a quite different direction. We can make it resemble Cl or Br in properties.

The group $-\text{N}_3$ possesses a remarkable resemblance to the halogens. Thus N_3-H is like $\text{Cl}-\text{H}$ a strong acid, and gives rise to a whole series of salts which closely resemble the corresponding halides.

We have thus succeeded in so modifying the attractive power of the nitrogen atom by operating upon it by means of suitable radicles, that on the one hand we make it behave like a metal such as K, and on the other like a halogen.

If we follow these operations by means of surfaces, the modification in the properties of nitrogen above described would be geometrically equivalent to deflecting the characteristic surface corresponding to uncombined nitrogen on the one hand, into a surface of a shape similar to that of the characteristic surface of

*) Mendelèef. Principles. Chem. 1. 254. (1897).

potassium, and on the other hand, into a surface of a shape similar to that of the characteristic surface of chlorine.

Sulphur.

In the radicle $(\text{CH}_3)_3\text{S}$ — the sulphur possesses the properties of a metal like K. For example the compound $(\text{CH}_3)_3\text{S—I}$ is like K—I a white crystalline soluble body.

By replacing the I by OH we obtain the base $(\text{CH}_3)_3\text{S.OH}$. This is as strong a base as KOH and resembles the latter to a remarkable degree, for example it absorbs carbonic acid, drives out NH_3 , cauterises the skin, and gives salts with acids with the evolution of heat &c. &c.

Moreover it yields salts with hydrogen sulphide which are extremely like the alkaline sulphides — eg. they dissolve antimony sulphide.

$$\begin{array}{c} \text{CH} = \text{CH} \\ \text{On the other hand in thiophene} \quad > \text{S} \text{ divalent sulphur} \\ \text{CH} = \text{CH} \end{array}$$

assumes the properties of the radicle $—\text{CH} = \text{CH}—$. “The replacement of the group C_2H_2 in Benzene by sulphur changes its properties so little that the preparation and properties of Thiophene derivatives in part agree almost word for word with those of Benzene.” *)

It thus appears that by operating on S with suitably chosen elements or radicles we can make it behave like a metal such as Na or K. By combining it with carbon in the benzene ring we can make it resemble and play the part of the organic radicle C_2H_2 .

Nitrogen, phosphorus, arsenic, antimony.

These 4 elements do not even superficially resemble each other. Combine each with three atoms of H, and we get the 4 compounds NH_3 , PH_3 , AsH_3 , SbH_3 , which have only a very faint resemblance to each other, so that in the words of Hofmann.***) “On comparing the terminal points of the series CH_3 and SbH_3 we cannot fail to be struck with the dissimilarity of the compounds which at first glance seems to limit the analogy between the two

*) van't Hoff. “Lectures on Phys. Chem.” III. 143.

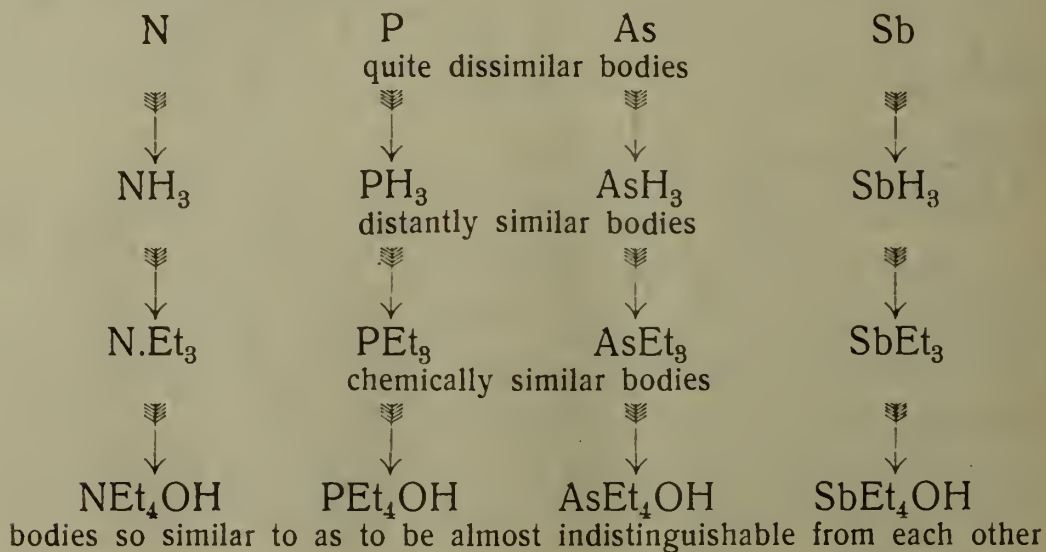
**) Phil. Trans. June. 1857, 575.

compounds to a mere parallelism of formula. Replacing the H by methyl or ethyl increases their resemblance — the intensity of the chemical tendencies being in general so much raised that the graduation of chemical properties is no longer perceptible to the same extent."

The addition of a methyl and a hydroxyl group still further increases their resemblance, so much so that Hofmann writing of the bodies thus formed, of the type $R.Et_4.OH$, expresses his astonishment that such dissimilar elements as N, P, As and Sb could produce such similar compounds:

"In these remarkable bodies P, As, Sb and N appear to play almost the same part. It is more especially in the oxides of these compound metals that analogy of composition induces a perfect identity of properties — the same salient properties being traced in every direction. If we were satisfied by a study of the reactions of these bodies we would never expect that in such similar compounds so different elements as N, P, As and Sb are. They might moreover be confounded with KHO or NaOH, by which they are scarcely surpassed in alkaline power. Only the deportment of the hydrated oxides under heat distinguish the derivatives of N from those of P, As and Sb. The N compound being more stable." *)

The transformation of properties by the addition of radicles may be exhibited thus:



*) Hofmann and Cahours, Phil. Trans. June. 1857. 575.

Geometrically expressed by means of surfaces, the successive modification of properties above described would resolve itself into the gradual transformation of the 4 dissimilar characteristic surfaces belonging to the 4 dissimilar elements N, P, As, Sb, into 4 similar surfaces belonging to the similar compounds NEt_4OH , PEt_4OH , AsEt_4OH , SbEt_4OH .

Iodine.

Iodine, especially in a monovalent condition, possesses under ordinary circumstances the properties of a halogen such as Cl or Br. By combining it with two phenyl groups we cause it to change its properties.

It now acts like a heavy metal such as thallium and lead. It produces a strongly alhaline base $\text{C}_6\text{H}_5\text{C}_6\text{H}_5\text{I.OH}$ analogous to TlOH , which in its turn produces a whole array of salts resembling closely the corresponding compounds of Pb and Tl. For example the sulphate is soluble and the haloid salts are precipitates, which appear exactly like the chlorides, bromides and iodides of lead and thallium. The sulphide is a precipitate which looks exactly like freshly precipitated antimony sulphide.*)

Hence just as the light atom of N by combining it with H or methyl can be made to resemble a light metal like K, so also the heavy atom of I by combining it with phenyl, can be made to resemble a heavy metal such as Pb or Tl. It thus appears that by operating on the iodine atom with suitable radicles we can so greatly alter its attractive power as to cause it at pleasure to display either the properties of a halogen like Cl or the properties of a heavy metal such as Tl or Pb.

If we follow the process by means of surfaces the operation would consist in deflecting a surface of a form similar to that of the characteristic surface of chlorine into a surface of a form similar to that of the characteristic surface of lead.

*) Victor Meyer. Ber. 26. 2122. 27. 509. (1893—94).

Modification of the attractive power of atoms by operating on them by heat, pressure, &c.

We have seen that by operating on elements by means of suitably chosen radicles we can modify their attractive power and therefore their properties to almost any extent. Now there are other influences besides the presence of other atoms which can modify the attractive power of atoms, and so modify their properties (§ 2 chap. I).

The temperature at which they are viewed, the pressure to which they are subjected, the medium in which they are immersed are all influences of this nature.

The question arises cannot we by operating on various elements with the temperature, pressure, media &c. alter their properties to quite as great a degree as when we operate on them with other atoms?

Cannot we for example by viewing different elements under different sets of conditions as regards temperature, pressure, medium &c. make them resemble each other, although perhaps when viewed under the same common conditions of temperature and pressure they do not in the least resemble each other? If by the action of discontinuous factors (such as the addition of atoms must necessary be since each successive atom introduced alters the properties in jumps, as it were) we can cause the most unlike elements to exhibit an astonishing degree of chemical resemblance, surely, by the application of continuous factors such as the temperature and pressure — factors which we can moderate or intensify to any required degree — we could produce an even greater degree of resemblance between different chemical elements?

That the properties of every element do change in a profound and indeed startling way with the temperature and pressure is undeniable.

For instance carbon of ordinary temperature is a perfectly inactive element. It refuses to combine with any other element, nor will it dissolve even in the strongest acids. It is in fact an inactive element like nitrogen. Yet it completely changes its nature at a high temperature. At a red or a white heat it becomes

one of the most chemically active elements known, displacing metals from their combinations with oxygen and freely combining with S and O. At the temperature of the electric arc its properties enter into a new phase. It now seems to become almost metallic in nature.

It conducts the electric current and dissolves freely in metals to form the somewhat indefinite carbides, much as metals dissolve in each other at lower temperatures to form alloys.

Other elements, too, change their nature in a way quite as remarkable. Nitrogen for example is quite as chemically active at a white heat as is oxygen at ordinary temperatures — combining with metals such as Ti, B, Mg, Ur, with the evolution of heat and light. At the temperature of the electric arc it even burns in oxygen forming a true flame in which platinum can be melted.

An alteration of pressure produces almost as great changes in the properties of bodies as an alteration of temperature. For example did we happen to live not under a pressure of one atmosphere but under a pressure of thousands or even hundreds of thousands of atmospheres — such as exist on some stars — the whole world of chemistry would change its features. The chloride of silver so stable under ordinary pressures would become unstable and evolve chlorine, decomposing into subchlorides — behaving in fact under these conditions much as MnCl_3 or PbCl_4 do under ordinary pressures.**) Multitudes of compounds so unstable at ordinary temperatures as to be unknown would become bodies of great stability. Chemical actions which occur so slowly at ordinary pressures as to be imperceptible would increase a million fold their velocity, eg. sulphur would inflame in air at ordinary temperatures, ignite when mixed with cuprous oxide, and become as chemically active at ordinary temperatures as otherwise it becomes at a red heat when viewed under ordinary atmospheric pressures.**)

Solids would react on each other as do fluids at ordinary pressures. Spring has shown that under very great pressures a mixture of carefully dried powders of potash, saltpetre, and sodium

*) Carey Lea. *Amer. Jr. Sc.* (3). 43. 527—531.

**) Spring. *Archives Neerlandaises*, 6. 257—261.

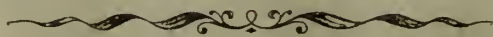
acetate react together and interchange their metals. In fact under vast pressures the most rigid solid bodies yield and flow like mobile liquids. The medium in which bodies are immersed also alters the intensity of force with which atoms attract each other.

In fact the same external temperature can produce a greater effect on bodies when immersed in some media than in others. For example a temperature of about 20°C acting on IrS_2 when immersed in a watery medium is sufficient to decompose it partially, at least, into Ir_2S_3 and sulphur. When however the same substance is immersed in a medium consisting of CO_2 gas an external temperature of 20° is powerless to effect it — a temperature above 100° being necessary to effect the same decomposition.

When surrounded by water vapour, a temperature of 350° will resolve NH_4Cl completely into NH_3 and HCl . In the absence of water vapour, however, the NH_4Cl is undissociated at the same temperature.

The molecules of H_2O_2 are very much more stable when surrounded by molecules of ether than by molecules of water.

So that by transferring H_2O_2 from an aqueous medium to an ethereal medium (by extracting the aqueous solution with ether) produces the same effect as regard the stability of the H_2O_2 molecules, as a lowering of temperature. It seems as if in watery media the attraction between atoms is weakened; in alcohol or ether it is increased. And this is a general phenomenon. For example, carbon does not combine with nitrogen directly at temperatures lower than that of the electric arc. But in the presence of metals or alkaline carbonates it combines with it at red heat; so that the carbon atom in the presence of metals or metallic carbonates is brought into the same state at a red heat as regards capacity for reacting on N, as the temperature of the electric arc brings about in their absence.



Chapter VII.

On the changes induced in the properties of elements by viewing them under other external conditions than those common in the laboratory.

The human mind has an innate tendency to regard every quality and every quantity as discontinuous and unalterable.

For instance, our whole conception of number depends upon this mental peculiarity.

The vast mathematical fabric which has been erected upon the theory of equations ultimately depends upon the possibility of finding certain constants which will reduce certain algebraical expressions to zero — the so-called roots of the equation.

Another great branch of analysis, the invariant theory, depends upon the possibility of making these same mathematical expressions assume, not zero, but a constant value, in whatever way the variables are changed.

In science this tendency shows itself in a thousand ways. For example, we are always unconsciously endeavouring to find some rigid distinction between men and animals, animals and plants, and even between different races of men — distinctions which invariably break down as our knowledge increases.

In chemistry this human weakness is very marked. Chemists are ever, and vainly, attempting to attribute fixed and permanent characteristic constants to the different bodies which come under their hands.

For example, the boiling-points and melting-points of compounds were once assigned the proud position of invariable con-

stants. Later, it was found that these are in reality not constant, but depend upon the external pressures to which the bodies are subjected. The colour of a compound was until lately thought to be an invariable characteristic; now we know it alters with the temperature, becoming, as a rule more intense with increase of temperature, and fading into whiteness at very low temperatures.

The metallic or non-metallic condition of an element is at the present time firmly believed by chemists to be a fixed and permanent characteristic, uninfluenced either by temperature, pressure, electric strain, or any other conceivable influence which can be brought to bear upon the element.

So that, because oxygen happens to be a non-metal, and sodium a metal, under those particular temperatures and pressures under which the chemist lives is for him a sufficient reason for believing that oxygen will continue to remain a non-metal, and sodium will continue to remain a metal under every other conceivable physical condition to which these two elements can be subjected — in my opinion a very improbable supposition.*)

The atomic weight of an element is believed to be an absolutely unchangeable constant of an element; though why everyone should be so absolutely cocksure about this matter it is hard to say because nobody has yet carried out very accurate weighings under temperature conditions greatly different from 18° C. In fact, no one knows anything about the matter.

We invariably find that as science advances these so-called constants are not really constants, but are variables which, under the conditions which we live and work, are very nearly constant.

It may be gravely doubted whether any quality or any quantity associated with a body is really permanent and unalterable. When James Thomson proved that what was formerly believed to be an eternal and unchangeable constant of nature, namely, the melting-point of ice, was in reality a variable depending upon the external conditions of temperature and pressure,

*) See a series of papers by the author *Chem. News* (1902). 86. 295; 87. 74, 162.

he caused in the scientific world a shock of surprise as great as would be caused at the present time were some one to prove that the atomic weight of oxygen altered with the temperature and pressure.

What we intend to discuss in this article is the changeability or unchangeability of the properties of elements.

A chemist at the present time piously believes that the properties of an element, as described in the text-books, are fixed and unalterable characteristics of that element, principally, by the way, because he has never reflected on any other possibility.

Thus we read that chlorine combines vigorously with sodium, does not act on carbon, produces a very explosive compound with nitrogen, &c.; and the young student of chemistry learns painfully by heart the chemical peculiarities of O, S, N, &c., in the fond belief that they are eternal and unchangeable characteristics of those elements.

As a matter of fact, they are but the particular phase of properties which those elements exhibit under the conditions under which we live and work. Under other conditions their properties are entirely different. For example we read that H and O gases, when heated together, combine with the evolution of heat and light to produce water. This is, however, only within a moderate temperature range. Did we happen to live at a temperature of $10,000^{\circ}\text{C}$, H and O would be described in the text-books as capable of existing together as a non-inflammable mixture, such as N and O gases at ordinary temperatures.

Carbon and silicon at ordinary temperatures are quite dead and inert. At a red or a white heat they wake up and become perhaps the most active substances known.

Fluorine at a very low temperature relapses into a state of chemical deadness, but at ordinary temperatures it sears the face like the vapour of white-hot steel. Nitrogen itself, so dead and inert as it appears to us, becomes a body of great chemical activity at high temperatures — inflaming, for example, in O at the temperature of the electric spark.

Chromium or iron, when made positive pole of an electric battery, assumes the properties of a noble metal, like Pt or Au;

made negative pole and they resume their ordinary properties.*) Nitrogen, subjected to a silent electric discharge becomes chemically active. Oxygen, under the same conditions, becomes enormously more active. Such examples can be multiplied indefinitely.

There are but two ways of regarding this matter: Either the properties which elements happen to exhibit under ordinary conditions of temperature and pressure are unalterable, or they are not.

The evidence is, I think, overwhelmingly against the first view. The properties of an element do undoubtedly alter, and alter very considerably according to the conditions under which it is viewed.

That the properties of an element should alter with the external conditions under which it is viewed is not very surprising when we consider that the chemical properties an element exhibits depend entirely upon the different forces with which it attracts the different kinds of atoms. And it is almost universally believed that the chemical force which an atom exerts on other atoms depends in some way or other upon the arrangement or motion of the electrons which it contains. If, then, we subject an atom to external strains, which alter the internal arrangement or motion of its electrons, then we alter at the same time the external attractive forces which the atom exerts on other atoms, and so alter the way it reacts chemically.

The temperature, electric field, probably pressure, medium, &c., are all influences which could conceivably affect the motion of the electrons within the atom, and thus affect the attractive forces of the atom.

In fact, we are probably not going too far when we suppose that the properties an element exhibits depend to a very great extent upon the external conditions to which it is subjected.

However this may be, it is certain that if we conclude that the chemical properties of an element do alter with the external conditions, such as the temperature, then we must also conclude

*) Hittorf. „Über das Verhalten des Chroms“. Zeit. für Electrochemie, 1899, No. 1.

that there is some law, simple or complex, which regulates this change.

For the change must take place in some definite manner or other, whether that manner be complex or simple, since the element invariably returns again to its original condition when cooled to its original state.

Does there exist a simple law regulating this change?

As a suggestion to be seriously considered in this connection, I venture to put forward the view that the properties presented by any element at ordinary temperatures are only particular phases or conditions which can be assumed by other elements also under other and as yet unknown conditions, and that our notions of the rigidity and unchangeability of the properties of elements are completely false, and arise to a great extent because of the experimental difficulties of accurately studying the properties an element exhibits under temperature and pressure conditions very different from those which hold in the laboratory and on the earth.

Those to whom our suggestion appears most incredible are precisely those who are most ignorant of the remarkable changes which sweep over the properties of elements when viewed at high or low temperatures and in the electric field.

It should be remembered that men were once in precisely the same mental condition as regards their views of the liquid, gaseous, and solid states in which different substances find themselves when all are viewed under the same conditions of temperature and pressure, as are chemists at the present time as regards their conceptions of the different chemical states which elements find themselves in when all are viewed under the same external conditions.

Yet we all know now that the solid, liquid and gaseous conditions of matter are only particular phases or conditions which can be assumed in succession by any substance by altering the external conditions of temperature and pressure under which it is viewed.

So also I suggest that the different chemical states which different elements find themselves in when all are viewed under

ordinary conditions, are merely particular phases or conditions which any element can assume in succession by altering in an as yet unknown way the various external conditions under which elements are viewed.

It should, however, be remembered that the temperature and pressure exert a great influence on the physical state (e. g., liquid, solid, or gaseous state) which a body finds itself in, because these are the influences which most affect particles of a molecular scale of magnitude.

But the change in the properties of elements depends upon the possibility of effecting matter when in a still finer state of division — the sub-atomic state of Crookes — so would be most affected, not by the temperature or pressure, but by finer influences analogous to the temperature and pressure — “sub-temperatures” and „sub-pressures“ we will called them.

In fact, just as different compounds have comparable temperatures and pressures — temperatures and pressures which bring them into the same physical state, so also different elements may have comparable “sub-temperatures” and “sub-pressures” which bring them into the same chemical states.

All this might appear at first sight very alarming, but it is not impropable. We are, in fact, upon the dawn of a new and grander chemistry than that which the older chemists contemplated.

Indeed, I think that it is undeniable that certain substances can be made to resemble each more closely in properties, chemically and physically, even by the operation of such a coarse influence as the temperature. And doubtless a closer resemblance could be obtained by altering other variables simultaneously, such as the electric field, pressure, surrounding medium, &c.

Let us give some examples:

Oxygen and sulphur.

O and S, viewed both at a common temperature, are in quite dissimilar chemical states. If, however, we view the O at ordinary temperature and the S at some 800—1000° C, the resemblance is greatly increased:

1. O and S, viewed both at ordinary temperatures, are in quite dissimilar physical states; the O is a very volatile gas, the S a solid. S viewed at, say, 1000° would become a volatile gas, just as O is at ordinary temperatures.
2. At ordinary temperatures the O molecule is O_2 and the S molecule is S_8 . If, however, we view the S at, say, 1000° , its molecules have the same composition (viz., S_2) as the O molecule at ordinary temperatures.
3. Oxygen is very much more chemically active than S, both being viewed at ordinary temperatures. At 1000° C S is quite — nay, more — chemically active than O at ordinary temperatures.
4. The majority of the compounds produced by S at ordinary temperatures have no analogies among O compounds.

For example, while H_2SO_4 , H_2SO_3 , and SO_3 are quite stable at ordinary temperatures, the corresponding O analogues are too unstable to exist. If, however, S be viewed at 1000° , these compounds would become quite as unstable as the corresponding O compounds at ordinary temperatures; SO_3 , H_2SO_4 , and H_2SO_3 all decomposing at a red heat.

At lower temperatures, however, O would probably assume the same condition that S assumes at ordinary temperatures. Probably complex compounds of oxygen, corresponding to H_2SO_4 , SO_3 , &c., are capable of existing at lower temperatures.

Indeed, the allotropic modifications exhibited by S at ordinary temperatures would probably be paralleled by O at low temperatures. Even at ordinary temperatures two allotropic modifications (against some eight or nine known for S) of oxygen are known, viz., O_2 and O_3 . At still lower temperatures the number of these allotropic modifications will probably increase. The field of low temperature research is an unexplored world.

The Halogens.

The same appears to be the case with the halogens. Fluorine seems to be in the same chemical state at ordinary temperatures

as Cl at a higher temperature. F, in fact, performs a great number of reactions at ordinary temperatures which Cl can not, but which it can when heated up.

For example, metallic Ur burns in F at the ordinary temperatures, in Cl at 180° , and in Br at 210° . So that F behaves towards Ur at ordinary temperatures just as Cl at 180° and Br at a higher temperature. A similar relation appears in their behaviour with a vast number of other substances. It is, in fact, a general phenomenon.

So that by viewing simultaneously F at an ordinary temperature, Cl at about 180° and Br at a higher temperature, we would make them all resemble each other chemically much more closely than by viewing them all simultaneously at a common temperature.

Notice that here again (as with O and S) those conditions which seem to render substances chemically more alike also render them physically more alike. For example, Cl and Br are at 180° and 210° as perfectly gasified as is F at ordinary temperatures. Viewed all at a common temperature, say, 0° C., this is not the case; F being a volatile gas, Cl an easily condensible vapour, and Br a liquid. It seems as if the same factors which determine the chemical similarity of bodies also determine their physical similarity.

Oxygen and the Halogens.

Viewed all at a common temperature, hydride of oxygen, viz., H_2O , differs very widely in properties from the hydrides of chlorine, bromine, and fluorine, HCl , HBr , and HF . And presumably for the same reason that oxygen differs widely from chlorine, bromine, and fluorine when viewed at the same temperature.

If, however, we view the water at high temperatures and the haloid acids at ordinary temperatures, or the water at ordinary temperatures and the haloid acids at low temperatures, the resemblance between them is greatly increased, and presumably also, the resemblance between O and the halogen under these conditions is greatly increased.

For example, viewed all at ordinary temperatures, we find that though metals dissolve in HCl or HBr, evolving H and forming salts, they do not, as a rule, dissolve thus in water.

If, however, we view the acids at ordinary temperatures and the water at, say, 200—300°, we find both water and acids behave towards metals in the same way. In fact, water at 200—300° reacts with metals, evolving H and forming oxides in precisely the same way that HCl and HBr react with metals at ordinary temperatures, evolving H and forming chlorides and bromides.

Thus, although water at ordinary temperatures is a neutral substance, not reddening litmus, it seems (like HCl or HBr at ordinary temperatures) to become acid at a high temperature. For example, at 400° H_2O decomposes KCl, evolving HCl, just as H_2SO_4 decomposes it at ordinary temperatures.

Conversely, at low temperatures, HCl and HBr seem to react in the same way as H_2O at ordinary temperatures, becoming, like water, colourless liquids, incapable of reddening litmus, dissolving metals, or hydrolysing fats.

Notice that here again those conditions which bring water into a similar chemical condition as HCl or HBr also bring it at the same time into the same physical condition. For example, H_2O , viewed at ordinary temperatures, is a liquid, while HCl and HBr are gases. But water viewed at 300° is, like HCl and HBr at ordinary temperatures, a gas. Conversely, water at ordinary temperatures and the acids at low temperatures are all liquids. Now, these observations apply not only to the hydrides of O, Cl, and Br, but in general to their other binary compounds also; e. g., the metallic oxides are, as a class, more stable and less fusible and volatile than the corresponding chlorides and bromides, viewed all at the same temperatures.

If, however, we view the metallic oxides at a higher temperature than the corresponding chlorides and bromides, we tend more to equalise both their stability and their fusibility and volatility. We are, in fact, dealing with a general phenomenon common to the compounds of O and Cl.

In the preceding chapters we have shown that the chemical properties of elements depend solely upon their chemical affinities.

And their chemical affinities alter in relative strength and intensity as the temperature changes (and probably also they alter with the pressure, electric field, &c.).

If, therefore, we can arrange to view two different and dissimilar elements, A and B, under two different sets of external conditions, so adjusted as to cause the affinities which A exerts to be equal or proportional to those which B exerts, we would solve the problem of making A and B chemically similar.

Whether this can actually be done or not is at present unknown. The facts we have quoted, however, are suggestive. In this connection let me mention still another possibility. If we can take advantage of the changes in the attractive forces of elements caused by altering the external conditions under which they are viewed, and arrange to view simultaneously all the different elements of the Periodic System, each under a different set of external conditions, each separate set of conditions being so adjusted as to make each of the elements thus contemplated attract the same radicles with the same (or with proportional) forces, and thus to make all the elements simultaneously chemically similar, then we would arrive at a means of unifying and simplifying the Periodic System in a way that has hitherto not been dreamt of. Chemists, here again, piously believe in the permanency and unchangeability of their Periodic Law. That it holds approximately under ordinary conditions of temperature and pressure is to them (if they have even considered the matter) a reason sufficient to make them believe that it will hold under all other conditions of temperature and pressure. This may be so; but in my opinion it is almost infinitely improbable.

The Periodic System, as it appears to us, is only a particular case of a general relationship which exists between the atomic weights and properties of elements. For it is the particular relation which appears between these quantities when all the elements are viewed at one particular common temperature and pressure, the particular common temperature and pressure being that under which we live, namely, about 18° C. and about 760 m.m. pressure.

But it is by no means necessary (apart from the question of the chemist's personal convenience) to view all the elements under the same conditions of temperature and pressure. If a simple relation appears when this is done, then some relation will probably hold under whatever way the temperature and pressure are altered.

It is quite as probable as not that a very much more simple law would appear by viewing, in the way we have suggested, each particular element under a particular temperature and pressure, a definite law being supposed to regulate the temperatures and pressures under which the various elements are viewed.

For example, it is conceivable that we might make all the elements chemically similar, and thus get rid of the groups and series of the system. Or we might arrange the conditions so as to make a continual and progressive alteration of properties of the elements with increase of atomic weight, and thus again get rid of the Periodic nature of the relationship altogether.

However, this may be, it is certainly desirable that the Periodic Law should be viewed not only under atmospheric conditions, but also under a series of other temperature and pressure conditions and the law of variation found.

Indeed, as regards the various elements we are in a condition altogether analogous to that which the older chemists were in towards the various gases. For just as Boyle's law, $PV = \text{constant}$, is the law connecting the pressure and volume of gases, viewed at a constant temperature, so also the Periodic Law is the law connecting the atomic weights and properties of elements all viewed at a constant temperature. And just as Boyle's law is no longer true when the temperature is made to vary, but is a particular case of a wider law expressed by—

$$PV = RT,$$

so also the Periodic Law probably does not hold true when the temperature is made to vary, but is a particular case of a wider law, and probably a very simple law.

I have spent more than two years studying the available data for comparing the elements and their compounds as they appear at high temperatures, with a view to discover such a law. I have,

however, failed to trace such a law, but strongly suspect that the heavy elements, such as Pb or Tl of a group of the Periodic System, are pictures of the chemical conditions which the lighter elements assume if viewed at a high temperature. So that at very high temperatures N and P would enter into a chemical condition, such as is presented by the heavier elements, Sb and Bi, of the same group, viewed at ordinary conditions, and that if viewed at still higher temperatures would enter into a radioactive condition, such as radium presents at ordinary temperatures.*) So that if we view the different elements of Mendeleeff's Periodic System, the lightest series at the highest temperatures, and the heaviest series at the lowest temperatures, we might in this way reduce to uniformity the Periodic System.

Data is, however, wanting, and will be wanting for many years to come.

I will now mention some other considerations which support the suggestion that the properties an element exhibits at ordinary temperatures, are only phase which under other external physical conditions can be assumed by all other elements also. I will discuss in the light of this conception the connection between metals and non-metals.

A general study of the Periodic Table shows that in any one group an increase of atomic weight almost invariably causes metallic properties to appear. This is well seen in the case of the group elements, C, Si, Ge, Sn, Pb, of Group IV., and N, P, As, Sb, Bi, of Group V.

In each case it seems that there is a gradual transition, with increase of atomic weight, of the non-metals into metals. The same relationship holds in almost all the other groups.

Now, it is a very remarkable fact that, in the case of the elements of the odd series at any rate, when an increase of atomic weight brings out metallic properties, it produces also at the same time a similar effect on the chemical behaviour of the elements as an increase of temperature.

*) See a series of papers by the author; Chemical News; 1901, lxxxiii., 130, lxxxv., 205, 310.

To illustrate this, let us take the case of the elements C, Si, Ge, Sn, and Pb.

Carbon and silicon at ordinary temperatures are very stable in a tetravalent condition, and extremely unstable in a divalent state. But as the atomic weight increases, the divalent condition becomes more and more stable, and the tetravalent condition more and more unstable, until finally, in the case of lead, the divalent condition is far more stable than the tetravalent condition, as appears at once manifest on contrasting PbCl_4 with PbCl_2 , and PbO_2 with PbO .

Now, this is precisely the same effect as an increase of temperature alone would bring about. Almost invariably the higher the temperature the more more and more do elements tend to pass from a higher to a lower grade of valency.

Iron, for example, at ordinary temperatures is very stable in the Fe''' state, and unstable in the Fe'' state, as at once appears when we contrast FeCl_3 with FeCl_2 . But at a very high temperature the Fe''' state becomes unstable, and the Fe'' state stable, the FeCl_3 passing spontaneously into FeCl_2 . This is the case with most other elements also; in fact, it is a general phenomenon.

On reflecting on these matters, it occurred to me that if an increase of atomic weight acts in the same way as an increase of temperature, would not, conversely, an increase of temperature act in the same way as an increase of atomic weight?

So that if an increase of atomic weight causes non-metals to pass gradually into metals, would not also an increase of temperature produce the same effect?

In other words, would substances that are non-metals at ordinary temperatures assume metallic properties at a very high temperature?

If this be so, a non-metal is nothing more or less than a substance viewed at a temperature too low for it to assume metallic properties; and, conversely, a metal is a substance viewed at a temperature too high for it to assume non-metallic properties.

So that the metallic and non-metallic conditions are simply phases, which all kinds of matter pass through as the temperature increases from zero upwards. If, therefore, we could only cool

down a metal, such as copper, to some exceedingly low temperature it would become a non-metal, just as glass is at ordinary temperatures, and refuse to conduct electricity; while, conversely, if we took the non-metallic carbon and heated it up to an excessively high temperature, it would become a metal and conduct electricity.

Of course, this is a mere speculation. But the idea is a very fascinating one indeed, and, if true, opens out a whole vista of possibilities hitherto scarcely dreamt of.

Moreover, it is contradicted by no known fact. On the contrary, there exist a great and growing number of facts which appear favourable to it. For instance, we all know how enormously the electric conductivity of non-metals increases as the temperature rises. It is sufficient to recall here the enormous increase in the conductivity of the rare earths at a temperature above 800° , a fact, which Professor Nernst has utilised in his celebrated lamp. Carbon also increases enormously in conductivity. Prof. T. Gray (Proc. Roy. Soc., January 12, 1882) showed that an increase of only 300° C. caused the conductivity of the best insulating flint glass to increase nearly eight-thousand-fold!

Conversely, Callendar and Dewar have established the fact that the electrical resistance of metals does not continue to decrease as the temperature falls, but reaches a small and nearly constant value (Callendar, *Phil. Mag.*, 1899, xlvii., 217), and Lord Kelvin believes (*Phil. Mag.*, March, 1902) that a metal below 1° absolute is a perfect insulator of electricity, at 2° it shows noticeable conductivity, and at 6° it possesses high conductivity; in other words, he thinks that a metal at these low temperatures behaves precisely as a non-metal behaves at ordinary temperatures.

It may, of course, be objected that whereas the resistance of metals at ordinary temperatures steadily increases with rise of temperature, the resistance of non-metals continually diminishes, so that both kinds of matter act in this respect in a directly opposite manner.

But it must be remembered that our experiments in the case of non-metals have as yet been made over very limited temperature ranges. The molecules of metals, for example, at ordinary tem-

peratures consist of only single atoms; whereas those of non-metals consist almost invariably of several atoms bunched together. Before we can expect non-metals to behave like metals, we should have to heat them so highly that they too are reduced to the same molecular condition as metals at ordinary temperatures; and this only occurs at very high temperatures indeed, as Victor Meyer proved in the case of the halogens.

This idea of the mutual convertibility of metals and non-metals might appear at first sight somewhat startling. But this is due in great measure to the fact that we have been educated to regard metals and non-metals as two distinct and discontinuous kinds of matter. Yet this is not the case. Metals and non-metals are not separated by any arbitrary line of demarcation, but shade gradually and imperceptibly into each other. And this seems to proclaim the unity of both kinds of matter. Why, therefore, should they not be mutually inter-convertible?

It must be remembered the history of science is full of the gradual fall of all arbitrary lines of demarcation. For example, before the time of James Thomson the melting-point of ice was thought to be an eternal and unchangeable constant of nature. Yet we all know now that, like most other "constants", it is in truth a variable, depending upon the external conditions of temperature and pressure.

So also at the present time, the metallic or non-metallic nature is thought to be an unchangeable characteristic of an element. So that if an element happens at ordinary temperatures and pressures to exhibit metallic or non-metallic properties, as the case may be, it will continue to exhibit them under all other conditions of temperature and pressure.

Yet such a view is extremely improbable, and it gains nothing in probability when we reflect on the profound and indeed startling way the properties of every element changes with the temperature and pressure. For instance, carbon at ordinary temperatures is a perfectly inactive element. It refuses to combine with any other element, nor will it dissolve in the strongest acids.

It is, in fact, an inactive body like nitrogen. Yet it completely changes its nature at a high temperature. At a red or

white heat it becomes one of the most chemically active elements known, displacing metals from their combination with oxygen, and freely combining with H, S, and O.

While at the temperature of the electric arc, it attacks indiscriminately the metals, dissolving freely in them to form the somewhat indefinite carbides, much as metals dissolve in each other at low temperatures to form alloys. *Similia similibus solvuntur*.

Other elements, too, change their nature in a way quite as remarkable; sodium, for example, is quite chemically inactive at -80°C .

With these astonishing modifications in the properties of elements in mind, he would indeed be bold who would assert that it is impossible for a non-metal to change into a metal at a high temperature, or a metal into a non-metal at a low temperature.

A theoretical explanation follows directly from the theory of electrons. We must suppose that non-metals possess a greater specific attraction for electrons than metals, both being viewed at a common temperature.

So that in the case of substances which are in a non-metallic state, the temperature at which they are viewed is not sufficient to detach the electrons from their atoms, and cause them to wander freely in the inter-molecular interstices. Whereas, in the case of substances which are in a metallic state, the temperature is high enough.

In the first case (non-metals), an electric current is caused by the movement of electrons and the atoms to which they are attached (electrolytic conduction). Whereas, in the second case, the electrons move independently of the atoms (metallic conduction).

An increase of electric tension acts in much the same way as an increase of temperature in detaching electrons from the surfaces of atoms. So that during the passage of a disruptive discharge, a non-metal, such as glass, is converted into a metallic state. An increase of the electric tension, therefore, lowers the temperature at which non-metals pass into metals. The temperature

of conversion is lowered to the ordinary temperatures at the point when the dielectric breaks down under the electric strain.

We will now mention two particular cases which are well explained by our suggestion.

a) *C a s e o f S e l e n i o n*. Amorphous Se does not conduct electricity, but when heated rapidly it begins to conduct at 165 to 175° C, and the conductivity increases until it attains a maximum at about 217°.

If Se is heated for a considerable time to 200° and is then allowed to cool, the conductivity decreases as the temperature rises and increases as the temperature falls. According to Kalischer this observation seems to show that at about 200° C a variety of Se is formed which behaves like a metal, and that on cooling this form remains mixed with the ordinary crystalline variety, so that the conductivity depends on the relative quantities of the two forms and therefore on the temperature. High temperatures therefore tend to induce a metallic condition in selenion.

b) *C a s e o f H y d r o g e n*. One of the most remarkable facts in chemistry is the twofold nature of hydrogen. On the one hand, it behaves precisely as a metal in a vast number of its chemical relations; and on the other hand it exhibits equally decided non-metallic characteristics.

Its metallic properties are striking in the extreme:

1. It generates a whole series of salts—the so-called acids—which are perfectly analogous to the corresponding compounds of Na and K, except in so far as they are stamped with the peculiarities of hydrogen itself. Such compounds, for example, are capable, of electrolytic dissociation, the H playing precisely the same part as a Na or K ion.

It was such facts as these, as well as the other special chemical relations of combined H, that forced the great chemists of the preceding century—Faraday, Dumas, Daniell, Graham, and Andrews—to entertain the view that H was metallic in nature, and allied to K or Na.

*) W. Siemens. *Phil. Mag.* 159, 117.

2. When hydrogen enters into the structure of a compound it exercises the same effect on its properties as a light metal, such as Na or K, making in general an acid compound less acid and a basic compound more basic.

For example, phenol, $C_6H_5.OH$, is more acid in nature than hexylic alcohol, $C_6H_{13}.OH$; and benzoic acid, $C_6H_5.COOH$, is more acid than hexylic acid, $C_6H_{13}.COOH$.

Similarly, N_3H is an acid, but N_2H_4 and NH_3 are strong bases.

The same effect is produced by Na or K. For instance, $H.OH$ is neutral, but $H.ONa$ a strong base. The diminution of acidity which follows the replacement of H by Na is well seen in the malonic esters: $HOOC-CH_2-COOH$, $HOOC-CHNa-COOH$, $HOOC-CNa_2-COOH$.

3. When the elements are arranged in the order of their affinity for positive electricity (Nernst, Neumann), H actually occurs among the metals, between lead and tin, as the following series shows: Mg, Al, Zn, Cd, Fe, Co, Ni, Pb, H, Sn, Cu, Hg, Pd, Au (Neumann, *Zeit. f. Phys. Chem.*, 1894, xiv., 193, particularly pp. 222—223; vide also Nernst, *Ber.*, 1897, xxx., 2, 1547).

So that H is able to precipitate from their solutions such metals as Cu, Hg, Ag, Pt, Au in just the same way that Mg precipitates such metals as Zn or Cd.

This may be easily shown experimentally by immersing a small plate of Pd, saturated with H, in a solution of $CuSO_4$. The plate soon becomes covered with a lustrous layer of Cu (Lüpke's "Electro-chemistry", 1897 p. 166).

4. Moreover, the thermal effects produced by the combination of H with equivalent quantities of the successive elements P, C, S, N, O are in the same order as those produced by the combination of Na with the same substances. Whereas the order in the case of a non-metal, such as chlorine, is diametrically opposite (van't Hoff "Lectures," iii., 93).

5. In addition, Pd is able to absorb several hundred times its volume of H gas and still retain its lustre and general metallic appearance, as would be the case if the compound is a Pd-H alloy.

From these facts it will be seen that H in its chemical relations presents all the characteristics of a metal.

On the other hand, Dewar has shown that liquid hydrogen is quite non-metallic in nature, being a non-conducting, transparent, mobile liquid, resembling, in fact, a liquid hydrocarbon rather than a metal.

How then are we to reconcile this sharp contrast between the chemical and physical nature of H?

For it is indisputable that H at ordinary temperatures behaves as a metal in most of its chemical relations.

While it is equally indisputable that at a very low temperature, at its boiling-point for example, hydrogen possesses the properties of a non-metal.

Is not the solution of this riddle to be sought in my suggestion that a high temperature tends to bring out metallic properties, and conversely, a low temperature to bring out non-metallic properties, so that, although at ordinary temperatures and pressures H shows a marked inclination to exhibit the fundamental properties of a metal, yet, nevertheless, at -252.5° (its boiling-point) its metallic properties have entirely disappeared?

The idea is well worthy of consideration, inasmuch as it affords a very simple explanation of one of the otherwise most inexplicable facts in chemistry.

If the suggestion that a very low temperature would transform metals into non-metals, be correct, some extremely remarkable results follow as a consequence.

These we proceed to notice:

1. At some temperature above absolute zero all substances recognised as metals at ordinary temperatures would become almost incapable of conducting electricity. Lord Kelvin believes at the absolute zero that all substances are absolute non-conductors of electricity (Phil. Mag., March, 1902).

2. They would also become incapable of conducting heat, since a capacity for conducting heat in general is associated with a capacity for conducting electricity.

It is natural to infer that at the absolute zero to temperature all substances become absolute non-conductors of heat. This result was arrived at (and communicated to the Physical Society)

by Mr. Brinkworth and myself towards the end of 1901 as a consequence of the breach of the law of thermal equilibrium at very low temperatures (vide *Chemical News*, 1902, lxxxv., 194). This and some other equally remarkable results of the reasoning contained in that paper will be published later.

3. At these very low temperatures the bodies recognised as metals at ordinary temperatures would lose their metallic lustre, and become in most cases brightly coloured solids; presenting, in fact, an appearance similar to that presented by the non-metals sulphur or iodine at ordinary temperatures.

It must be remembered the colour of metallic substances is completely hidden by their metallic lustre. Yet most of these metals are undoubtedly very vividly coloured bodies.

For example, the vapour of sodium is violet just as the vapour of iodine is violet. Silver produces a blue vapour. Gold in thin layers transmits a greenish light. In a solid condition, therefore, and in such a state that the effect of their metallic lustre is eliminated, we should expect such substances to appear quite as brightly coloured as solid iodine or sulphur.

4. Since the valency bonds of a metal are of an electro-positive nature, while the valency bonds of a non-metal are of an electro-negative nature; then, if a metal can be transformed into a non-metal by simply lowering the temperature sufficiently, it follows that the difference between a negative and positive valency bond lies not in any absolute difference in the nature of the electrons (atoms of electricity), which are supposed to cause the phenomena of valency (*Helmholtz, Journ. Chem. Soc.*, 1881, xxxix, 277), but solely in the difference in the stability with which the electrons are held by the atom.

If these electrons are very firmly held by the atoms (non-metals) they give rise to what are known as negative valency bonds. If feebly held (metals) they give rise to positive valency bonds.

This conclusion is supported by other considerations.

(a). Carbon, a non-metal, is tetravalent, and therefore possesses four negative electrons condensed on its surface. Tin, a metal of

the same group, possesses four positive electrons, being also tetravalent.

If these valencies were in the two cases caused by two entirely different-in-nature entities (such as positive and negative electrons are often supposed to be), these two sets of valencies should behave quite differently. But this is not the case.

Tin combines with the same radicles as carbon (e.g., Cl, O, CH_3 —, C_2H_5 —, &c.), and produces corresponding compounds.

Not only is this so, but tin can actually replace optically active carbon in certain bodies and without the compounds losing their optical properties as Mr. Pope has shown (Journ. Chem. Soc., 1900).

This last case clearly demonstrates that the tin atom can combine with the same radicles as the carbon atom, and in such a manner that the individual radicles are attached to the tin atom in precisely the same way that they were attached to the carbon atom.

So that the four valencies of the tin atom produce precisely the same effect as the corresponding four valencies of carbon.

It is therefore highly improbable that the valencies of tin are produced by a cause diametrically opposite to that which produces the valencies of carbon, as would be the case were the so-called positive and negative electrons of an entirely different nature.

A similar argument applies to other groups of elements (e.g., the N—Bi group), and to replacement of H by Cl.

(b). The more heavily charged with electrons is an atom the greater the mutual repulsion the electrons exert on each other.

An addition of electrons to an atom, therefore, produces the same effect on the stability with which the electrons are held as an increase of temperature. In both cases the negative valencies should tend to become positive, if the positive or negative nature of a valency bond depends only on the degree of stability with which the electron producing that bond is held by the atom. A great many examples can be quoted showing that this actually does take place. In fact, it is a well known empirical generalisation that unsaturated radicles are electronegative and saturated

radicles usually electro-positive in nature. We quote two of the most striking examples.

Iodine. — The valency bond attached to monovalent iodine is strongly electro-negative (cf. KI, AgI, &c.). But when two additional electrons are added to the iodine atom the valencies become strongly electro-positive. For example, the residual valence attached to I in the radicle $\begin{smallmatrix} \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_5 \end{smallmatrix} > \text{I}—$ acts in the same way as the valence attached to the thallous atom, $\text{TI}—$ (V. Meyer, Ber., xxv., 205).

Nitrogen. — The valency bonds attached to trivalent nitrogen are strongly electro-negative. For example, the residual valence in the system $\begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} > \text{N}—$ can enter into combination with metals, and play the part of the negative valence of the system $\text{HO}—$, as appears manifest from the large number of metallic amido-compounds now known to exist.

But when we endow the nitrogen atom with two additional electrons (as in the system $\begin{smallmatrix} \text{Et} \\ \text{Et} \\ \text{Et} \\ \text{Et} \end{smallmatrix} > \text{N}—$), the residual valence changes

to sharply positive, the residual valence of the radicle $\text{Et}_4\text{N}—$ being as strongly electro-positive as that attached to an Na or K atom; $\text{Et}_4\text{N}—\text{OH}$ is, in fact, as powerful a base as NaOH. We thus arrive at the generalisation that one, and only one, kind of electrons cause the phenomena of chemical valence. The electrons can cause an atom to appear either as electro-positive or electro-negative in nature according as they are feebly or firmly held by the atom. This places us in a position to define the law of the special arrangement of the valence bonds on the surface of the atom. For electrons, being equally charged particles of like sign, repel each other with the same force.

Therefore in the case of a polyvalent spherical atom whereon several electrons are condensed by the attractive power of the material out of which the atom is composed, the mutual repulsion

between the electrons will cause them to take up a position of equilibrium on the surface of the sphere such that each is as far removed as possible from its neighbour, and if possible in a symmetrical position.

Therefore the manner in which the electrons (and, consequently, valency bonds) distribute themselves over the surface of an atom depends only upon the number of electrons, and not at all upon the nature of the material out of which the atom is composed. The problem, therefore, of determining the shape of an atom of valency n is reduced to the problem of distributing n points as symmetrically as possible over the surface of a sphere. We infer:

1. The shape of an atom depends only upon its valency. All atoms which possess the same number n of valency bonds have the same shape, provided that there exists only one way of arranging symmetrically these n points over the surface of a sphere.

2. When the valence of an atom changes, its shape also changes, and in a way that depends not at all upon the nature of the atom, but solely upon the final value of its valence.

We have deduced these generalisations by assuming the atoms on which the electrons are condensed are spherical. Even if this is not so, the same results hold approximately true on account of the very great repulsion the electrons are capable of exerting on each other.

The first of the generalisations is supported by the phenomena of isomorphism (Mitscherlich's law), though of course the result is only strictly true, when all the atoms or radicles attached to the central atom are identical, and attract each other with a force much less than the repulsive force which exists between the electrons by which they are attached to the surface of the central atom.

The second generalisation has, in a less general form, been already enunciated by Mr. Pope as a result of his experimental researches (Journ. Chem. Soc., 1900, lxxix., 828).

Alteration in the affinities of the elements with the temperature.

We will now return to the problem referred to at the end of chapter V — namely to the problem as to how the temperature effects the form of the affinity surfaces of the elements. Since a simple law (the wave law) regulates the affinities the elements mutually exert on each other when all are viewed at ordinary temperatures and pressures, then a law of some kind will probably regulate their affinities when they are viewed under any other conditions of temperature and pressure.

From the foregoing pages it will be seen that there is grave reason to believe that a high temperature tends to bring out metallic properties in an element, and a low temperature, non-metallic properties. If this be really so, it is clear, that as we gradually increase the temperature whereat the elements are viewed, the form of the affinity surfaces of non-metals would tend to shift over into the form of the affinity surfaces of metals; so that (see chap. V) increasing the temperature whereat the elements are viewed would tend to shift the wave crests of the affinity surfaces shown in the large plate at the end of the book, from left to right; while a lowering of temperature would tend to shift them from right to left.

The remarkable effect the temperature has of increasing the chemical activity of all elements is probably the outward manifestation of this shifting in their affinities — the affinities of an element for elements with which it is stably combined at ordinary temperatures becoming feeble as the temperature increases, and its affinities for other external elements becoming great. So that when the compound is heated to a high temperature and then brought into contact with the external elements, it is decomposed by them with inflammation, although perhaps when viewed at ordinary temperatures it is unacted on by them. It is clear, in fact, that the main consequence of this general shifting with the temperature of the affinities of one elements from elements of one kind to those of another kind would manifest itself in a tendency for compounds which are stable at ordinary temperatures to become

unstable at high temperatures; and conversely for compounds unstable at ordinary temperatures to become stable at high temperatures. The general decomposition of chemical compounds with the temperature is probably due not only to the increased kinetic energy of the atoms, but also, and often a very large extent, to an actual weakening in the chemical attraction which the atoms composing the molecule exert on each other.

As evidence for the correctness of my views, I will give a number of cases of compounds which although very unstable at ordinary temperatures become stable at high temperatures:

1. The case of Silicon Hexchloride, Si_2Cl_6 . — This substance is a colourless volatile liquid, which boils at 146°C . without decomposition. At 350°C . the vapour commences to dissociate, and the amount of dissociation continually increases up to 800°C ., when the compound is completely resolved into silicon and the tetrachloride, thus: $2\text{Si}_2\text{Cl}_6 = 3\text{SiCl}_4 + \text{Si}$.

Troost and Hautefeuille found, however, that if the temperature be quickly raised above 1000°C . that no dissociation occurred. The substance, therefore, is stable above 1000°C . and below 350°C ., but yet is incapable of existing at intermediate temperatures (vide Roscoe and Schorlemmer's "Chemistry").

2. Ozone, O_3 . — This compound is at ordinary temperatures very unstable, and is completely decomposed into oxygen gas at 250°C . Nevertheless Dewar showed ("Roy. Instit. Year Book", 1887-89, p. 559) that it could be produced at a white heat. His method was to heat up a platinum cylinder to a white heat, and pass a stream of oxygen gas through the tube. The oxygen gas thus heated was suddenly withdrawn and cooled by being sucked down by a stream of cold water circulating in an interior platinum tube. The resultant gas is said to have contained a large amount of ozone. From this experiment Dewar concludes that ozone has two centres of stability, and one of these is near the melting-point of platinum. Nernst*) shares this view and calculates that at 2103°C ., oxygen gas contains at

*) German Assoc. Cassel. 1903.

0.1% of O_3 ; at 3230° 1%, at 6400° it contains 10%, whereas in the sun the oxygen must be wholly in the form of ozone, owing to the high temperatures and enormous gravitational pressures. Just as at ordinary temperatures the power of self combination of carbon is most abnormally developed, so at high temperatures the power of self-combination of oxygen is perhaps most highly developed. This would mean that at a high temperature the crest of the affinity surface of oxygen has shifted from left to right until it lies over oxygen itself. At ordinary temperatures the crest lies over lithium on the extreme left hand side of the Periodic System.

3. Hydrogen Selenide, H_2Se . — This was investigated by Ditte in 1872 (*Comptes Rendus*). He showed that its dissociation first increased, then diminished until a minimum was reached and then again increased.

4. According to Ostwald (*"Outlines of General Chemistry,"* p. 312, 1890 ed.) cyanogen and acetylene are other examples. Both gases are formed in quantity at the highest temperature we can produce — in the electric arc and in the blast furnace. Yet at a red heat these gases cannot exist, cyanogen, as is well known, falling apart into its elements, whilst acetylene decomposes into other and more stable hydrocarbons, such as benzene.

5. Victor Meyer and Langer have shown that chlorine violently attacks platinum at a low temperature, but is without action upon it between the range 300° — 1300° C. It then again begins to attack the platinum, the attack becoming violent between 1600° — 1700° C. (*"Brit. Assoc. Reports,"* 1885, p. 961).

6. The metallic carbides at ordinary temperatures, are unstable bodies, usually endothermic, and often explosively decomposable by chemical reagents. At very high temperatures, however, they appear to be among the most stable of the carbon compounds. The attraction of carbon for metals seems to increase as the temperature increases, and decrease as the temperature falls.

7. $AuCl_3$ is a very unstable body at ordinary temperatures, and at about 200 — 250° C. is nearly completely decomposed.

Nevertheless Rose^{*)} shows that at very high temperatures its dissociation seems to retreat.

8. **RuO₄**. Ruthenium tetroxide, RuO₄, is formed by direct union at about 1000°, but decomposes on cooling. This is a most curious result, for the tetroxide is decomposed violently when heated to 108°, and it is only by rapid cooling by means of an inside tube through which cold water circulates, which passes through the outside tube, heated to bright redness, that it was possible to isolate some of the tetroxide without decomposition.

If allowed to cool slowly, the body dissociates again into Ru and O.^{**)}

There is some evidence that a similar volatile oxide of platinum exists, which is stable at high temperatures, but incapable of existing at lower temperatures.^{***)}

9. **Oxides of Nitrogen**. The oxides of nitrogen are all at ordinary temperatures extremely unstable, and below 800° all are apparently decomposed into N and O. But at the temperature of the electric arc. N and O not only combine freely, but combine with the evolution of heat and light, forming a true flame in which platinum can be melted.

A considerable number of other cases can be quoted. But the phenomenon is obscure and little understood.

These cases, be it noticed, were all discovered by accident. No systematic search has, so far as I am aware, been specially made to discover other examples and they are commonly regarded as anomalous. I would suggest, however, that they are but examples of a much wider law, and that probably under different physical conditions all compounds would exhibit analogous variations.

It must not be forgotten that hydrogen gas was once regarded anomalous in respect to its behaviour under pressure.

^{*)} Jr. Chem. Soc. (1895) **67**, 881.

^{**) Debray and Joly, Comptes Rendus. **106**, 100 and 228. See also *ibid.* **84**, 946.}

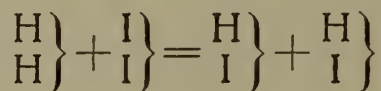
^{***)} See Hall. J. Amer. Chem. Soc. (1900) **22**, 494—501.

But the subsequent researches of Amagat showed that under suitable physical conditions all the other permanent gases behaved similarly.

The converse phenomenon, namely the steady decrease with the temperature in the stability of compounds stable at ordinary temperatures is too well known for it to be necessary to give examples. How this shifting in the value of the affinity would exhibit itself as regards the law governing the variation of the heat of formation of compounds with the temperature is easy to see.

If the compounds are exothermic and therefore stable at ordinary temperatures, their heats of formation would steadily decrease as the temperature increases until they become zero. Heating beyond this point would cause them to become endothermic. Conversely bodies which are endothermic at ordinary temperatures would become at a high temperature first possessed of heat of formation and then exothermic. So that the heat of formation of a compound would in some cases, at least, on account of the shifting of the affinity, be a periodic function of the temperature:

To see how this follows we have only to consider the case of hydrogen iodide. When H combines with I the change is not simply $H + I = HI$, but strictly speaking the change is a double decomposition, thus:



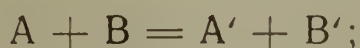
Now if the heat required to effect the separation of H from H, and I from I is greater than the heat generated when 2H combines with 2I, then the result will be negative. No heat will be given out, but a certain amount will be absorbed from external sources. This is the case with the heat of formation of HI at ordinary temperatures. If, however, the mutual attraction of the H atoms for the H atoms, and the I atoms for the I atoms diminishes; and the attraction of the H atoms for I atoms increases, at a certain temperature the heat required to separate H from H and I from I will be less than the heat generated when 2H combines with 2I. When this is the case,

the heat of formation of HI becomes positive. From this consideration, it is clear that if the affinities of an element for other elements shifts from elements of one kind to those of another kind, with the temperature, then, in certain cases at least, endothermic compounds will become exothermic at high temperatures, and, conversely, exothermic compounds endothermic.

That this supposition would explain the remarkable cases just given is made clear by the following investigation:

According to the modern theory of chemistry, the dissociation of a compound is a reversible chemical reaction. If, therefore, we assume that the positive or negative value of the heat of formation of certain compounds is a periodic or recurring function of the temperature, we can apply the laws of thermodynamics to investigate in what manner the dissociation will vary with the temperature.

Consider the gaseous reaction



where A and B are molecular species which, by reacting on each other, give rise to the molecular species A' and B'. Then, according to the law of mass action, the velocity of the change from the left to the right, in the sense of the above equation, is

$$v = k \cdot c_1 c_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

where c_1 and c_2 are the active masses of the reacting molecules A and B respectively, and k is the proportional constant. Similarly, the velocity of the reaction in the sense of the equation from the right to the left is

$$v_1 = k' \cdot c_1' c_2' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

But when a state of equilibrium has been arrived at

$$v = v_1$$

or

$$k c_1 c_2 = k' c_1' c_2',$$

denote

$$\frac{k}{k'} \text{ by } K.$$

Then

$$K = \frac{c_1' c_2'}{c_1 c_2} \dots \dots \dots (3).$$

K is the coefficient of equilibrium of the system, and it denotes how much faster the reaction proceeds in the sense of the above equation from the left to the right than from the right to the left.

This coefficient K varies with the temperature. This variation at constant volume is expressed by the equation derived from thermodynamical considerations by van 't Hoff

$$\frac{d \log K}{dT} = \frac{q}{RT^2} \dots \dots \dots (4).$$

T denotes the absolute temperature of the system, while R is the ordinary gas constant in the equation $pv = RT$ expressed in suitable units. It is advisable to thoroughly understand the nature of q . q denotes the total internal change in the energy of the system in consequence of the reaction.

If the molecular species A and B when reacting to produce A' and B' evolve heat, then the products of the change (A' and B') possess less internal energy than the molecular species whence they are derived, namely, A and B . q is in this case associated with a diminution in the total energy of the whole system, and consequently is negative. If, however, the products A' and B' are produced from A and B with the absorption of heat, then the products A' and B' are at a higher energy potential than A and B ; consequently, the reaction $A + B = A' + B'$ is associated with an increase in the total internal energy of the system, and it follows that q is positive. To sum up then, q is negative in the case of an exothermic reaction, and positive in the case of an endothermic reaction.

Re-arranging Equation 4 we obtain

$$d \log K = \frac{q}{R} \cdot \frac{dT}{T^2},$$

integrating

$$\log K = -\frac{q}{R} \cdot \frac{1}{T} + \text{constant}.$$

Let K_1 and K_2 represent the equilibrium coefficients of the system at two different temperatures T_1 and T_2 ($T_2 < T_1$). Further, suppose T_2 and T_1 to be close together, so that q will not change noticeably between the interval T_2 and T_1 . Then, substituting these values in the above equation and subtracting, we obtain

$$\log K_2 - \log K_1 = \frac{q}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \dots \dots (5).$$

Now, according to our hypothesis, q successively changes from a positive value (say) through zero to a negative value.

So long as r has a finite positive value, the expression $\log K_2 - \log K_1$ has also a positive value. Hence

$$K_2 > K_1$$

so long as the value of the equilibrium coefficient increases with the increasing temperature — although at a diminishing rate, as may be seen from the form of Equation 5. But K represents how much faster the system $A + B$ reacts to produce $A' + B'$ than the system $A' + B'$ reacts to reproduce $A + B$.

Consequently an increase in the value of K means that there occurs in the gaseous mixture we are considering a decrease in the amount of $A + B$ and an increase in the amount of $A' + B'$ present per unit volume. Consequently, with rise of temperature, q remaining positive, the reaction



tends more and more to cause the complete conversion of the A and B molecular species into the A' and B' species. Hence in those cases of dissociation which are attended by an absorption of heat — such as the dissociation of CaCO_3 , N_2O_4 , &c. — the dissociation becomes more and more complete as the temperature increases.

When, however, $q = 0$,

$$K_2 = K_1,$$

and so long as q retains this value a further increase of tempera-

ture does not cause the relative amounts of the species A and B, A' and B', in the system to vary.

But if q becomes negative, i.e., if the reaction $A + B = A' + B'$ is attended with the evolution of heat, as is the case when hydrogen and oxygen are heated together to a suitable temperature, then

$$\log K_2 - \log K_1 = \text{a negative quantity.}$$

That is

$$K_2 < K_1.$$

Hence with increasing temperature the system $A + B$ reacts to produce $A' + B'$ at a slower rate than the system $A' + B'$ reacts to reproduce the system $A + B$.

Consequently, with increase of temperature the amount of the molecular species A and B in the system continually increases at the expense of the A' and B' molecular species.

We thus arrive at the following law, which is known as van 't Hoff's Principle of Mobile Equilibrium:

If we heat a chemical system at constant volume, then there occurs a displacement of the state of equilibrium, and in that direction towards which the reaction advances with the absorption of heat.

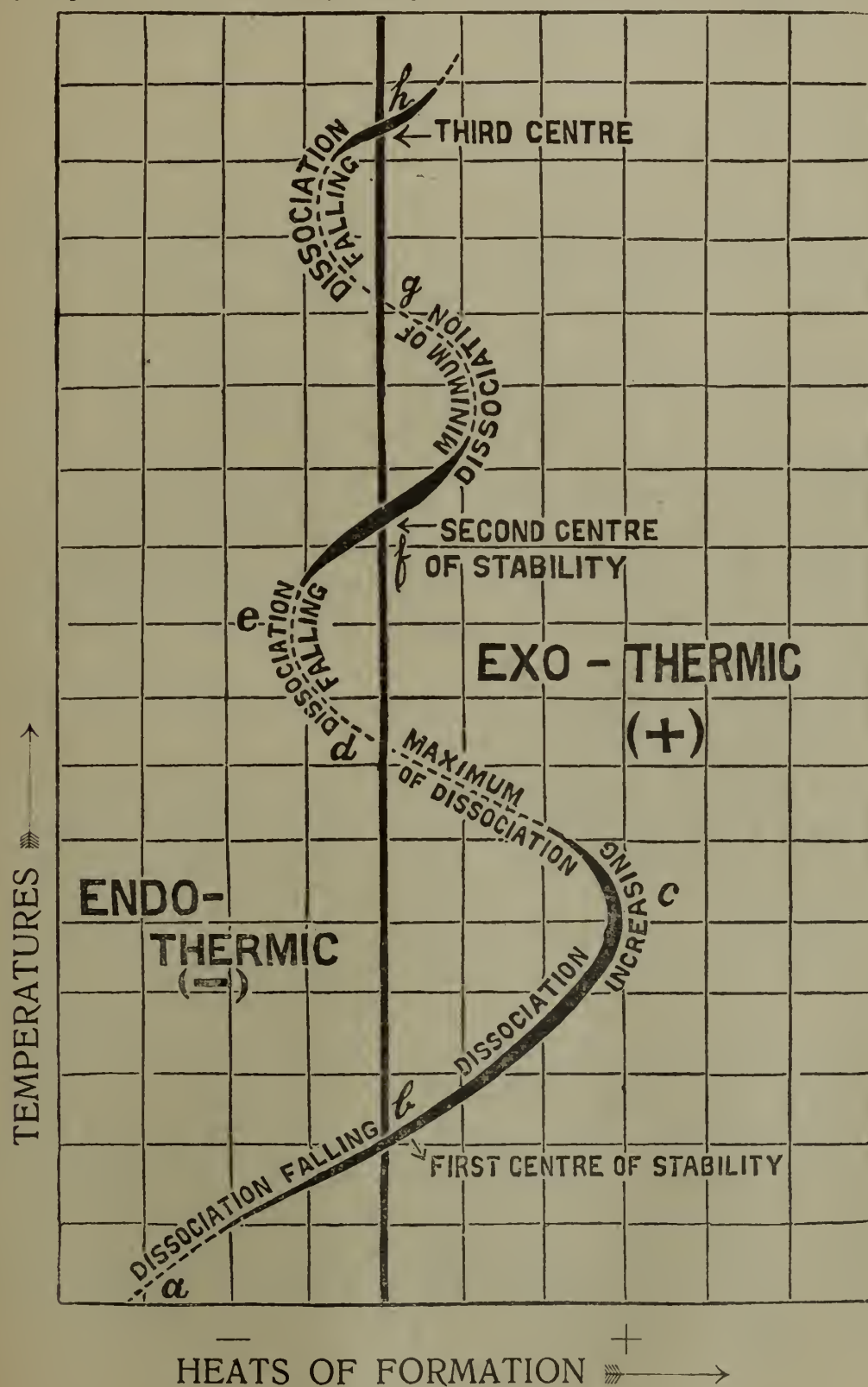
Assuming the truth of the supposition that the heat of formation of compounds is a periodic or recurring function of the temperature, we may draw such a hypothetical curve representing this variation in the value of q as is shown in Fig. 1.

The abscissæ represents the heats of formation of the compound, and the ordinates the temperature.

On applying van 't Hoff's "Law of Mobile Equilibrium", we deduce that from a to b the dissociation of the compound continually retreats. At the point b , where the heat of formation is zero, a point of minimum dissociation occurs. This point is therefore the first centre of stability of the compound.

On further increasing the temperature the dissociation will continually increase, and the compound becomes exothermic. But it will be noticed that there are now two opposing forces at work. From b to c the compound becomes more and more exothermic, and consequently more and more stable. Never-

theless, with the increase of temperature, the motion of the atoms in the molecule becomes more pronounced. Usually the increased attraction of the atoms for each other is greater than their tendency to fly apart, and consequently from *b* to *c* the dissociation in



many cases becomes practically negligible. Examples of such stable gases are ammonia and hydrochloric acid gas. On further heating, however, the heat of formation gradually diminishes, and consequently the increased motions of the atoms causes an increase in the amount of dissociation, which increases continually from c to d , and attains a maximum at d . In many cases the body is completely decomposed at d ; for example, silicon hexchloride.

At d the heat of formation again becomes zero, and further heating causes q to become negative. Consequently there is now a tendency for the atoms to aggregate together again, and this tendency increases continually with the temperature until the point f is reached. At f the dissociation will again be a minimum, and there will result a second "centre of stability" of the compound. By following up the curve we obtain a third centre of stability at h .

Of course one can hardly expect a gaseous body to exist all along the curve. In most cases it would probably only be capable of existing at certain points. The dotted part of the curve shows when the body would be most liable to be incapable of existing.

In all cases, however, we should look for the substance to appear at the points b , f , and h .

The examples above quoted, where a compound is capable of existing at a low temperature, and again at a high temperature, but not at intermediate temperatures, are thus well explained by our supposition.

The dependence of the heat of formation upon the temperature has been investigated in the case of very few endothermic compounds. Victor Meyer, however, in 1893, studied the case of hydrogen iodide. The heat of formation of this compound is -6100 calories. With increase of temperature, the negative value of its heat of formation continually diminishes until, at 324°C ., it becomes zero. At still higher temperatures it becomes positive. In this case, then, we have an example of an endothermic compound gradually changing into an exothermic compound.



Appendix A.

On the cause why compounds of a high valency grade often decompose into compounds of a lower grade, without giving rise to intermediate compounds.

In general the intensity of the force with which atoms are attracted by an atom A when the latter is in different valency conditions varies with the particular valency grade assumable by A. Sometimes the intensity of force exerted by A on each individual atom is greatest when A is in a high valency state. Sometimes it is greatest when A is in a low. Usually the higher the valency grade A finds itself in, the feebler the force it exerts on other atoms; for example, the chromium atom when in an octavalent state (Cr^{VIII}) exerts but a very feeble force on oxygen, CrO_4 evolving O at $20\text{--}25^\circ\text{C}$. In a hexavalent condition the force which the Cr atom exerts is considerably greater, CrO_3 evolving O at about 195°C . In a tetravalent condition the attraction which the Cr atom exerts is still greater. CrO_2 evolving O at 300° ; finally, in the trivalent condition the attractive force the Cr atom exerts on the O is enormous. — Cr_2O_3 not parting with O even at the highest temperatures.

Did the rule always hold true, it would be invariably easier to detach an atom from a molecule containing many atoms attached to a central atom A, than from one containing only a few atoms attached to A. This is not always the case; for example, trivalent Au attracts Cl with a greater intensity of force than monovalent Au; thermal data shows that this is so:

$$\frac{1}{3}(\text{Au}''', \text{Cl}^3) = 7.6 \qquad (\text{Au}', \text{Cl}) = 5.8$$

Also AuCl is easier to decompose, both by heat and water, than AuCl_3 . Similar cases are furnished by other elements; for example In''' exerts stronger forces on Cl than In'' or In^I , judged from the behaviour of the chlorides InCl_3 , InCl_2 , InCl ; Bi''' attracts Cl more strongly than Bi'' (in BiCl_3 and BiCl_2); C^{IV} attracts O more strongly than C'' :

$$\frac{1}{4}(\text{C}^{\text{IV}}, \text{O}^2) = 24.2 \qquad \frac{1}{2}(\text{C}'', \text{O}) = 14.5$$

I''' attracts Cl more strongly than I^I :

$$(\text{I}^I/3''', \text{Cl}) = 5.4; \qquad (\text{T}', \text{Cl}) = 2.1$$

Mo , Hg , Pt , and Ru atoms furnish further examples.

This is the reason why high grade compounds often decompose discontinuously to lower compounds without giving rise to intermediate compounds; for example I_2O_5 when heated decomposes at 300° directly into I and O , without forming lower oxides. The reason, of course, is that the iodine atom when in a pentavalent state attracts the O atom more strongly than when in a tetrad, triad, diad, or monad state; so that when the temperature is high enough to detach the O from IV in I_2O_5 , it will be still more easy to detach it from I^{III} in I_2O_3 or I' in I_2O ; hence I_2O_5 will pass directly into I and O without giving rise to I_2O_3 or I_2O . In fact I_2O_5 decomposes at over 300° ; IO_2 at 170° , and I_2O_3 at $125\text{--}130^\circ$. I_2O_5 is undecomposed by boiling water, whereas both IO_2 and I_2O_3 are decomposed, the former precipitating I , the latter evolving I and O .

In a precisely similar way MoO_3 when reduced by H passes directly into MoO_2 without giving rise to intermediate oxides, such as Mo_2O_5 or Mo_3O_8 . Rogers and Mitchell showed*) that Mo_3O_8 — an oxide intermediate between MoO_3 and MoO_2 — is more easily reduced than is MoO_3 or MoO_2 when heated in a stream of H . This shows that Mo^{VI} and Mo^{IV} attract O more strongly than Mo^{V} . Similarly, MoO_2 when heated in H , passes directly into Mo , without producing any of the lower oxides, such as MoO , Mo_2O_3 , or Mo_2O . Mo^{IV} , in fact, attracts O more strongly

*) Jv. Amer. Chem. Soc. 1900, 22, 350—351.

than Mo^{III} , Mo^{II} or Mo^{I} ; and hence any influence which is capable of tearing away the O from Mo^{IV} in MoO_2 will still more easily tear it away from Mo^{III} , Mo^{II} or Mo^{I} in Mo_2O_3 , MoO , or Mo_2O , where O is more feebly held. Similarly, $\text{Mo}^{\text{IV}}\text{S}_2$ when heated in a current of H, is reduced directly to the metal without forming a lower oxide.*) The case of potassium is remarkable. K forms 4 oxides K_2O , KO , K_2O_3 , and KO_2 , in which it is presumably in the four valency states K^{I} , K^{II} , K^{III} , K^{IV} . Yet the O is attached to the K with very different forces in each of these oxides; thus $\text{K}^{\text{II}}\text{O}$ and $\text{K}^{\text{IV}}\text{O}_2$ seem both stable states of aggregation, neither tending to oxidise nor decomposes at ordinary temperatures — KO_2 , in fact, only decomposes at a white heat; on the other hand the intermediate oxides K_2O and K_2O_3 are both remarkably unstable; indeed it is doubtful whether K_2O has ever been attained pure, while K_2O_3 when exposed to the air at ordinary temperatures, becomes incandescent and burns to KO_2 , and this although the still lower oxide KO is quite stable, dissolving in H_2O without decomposition and remaining unchanged when exposed to the air.

The most stable oxide of chlorine is Cl_2O_7 — the other lower oxides such as Cl_2O , Cl_2O_3 , ClO_2 , being all extremely unstable and explosive. Cl^{VII} attracts O more strongly than Cl^{I} , Cl^{II} and Cl^{III} . The preceding facts show that an element does not usually generate compounds which uniformly decrease or increase in stability as their valency grade increases. In fact it is a general phenomenon that as regards stability the compounds of an element separate out into two distinct groups — those of an odd and those of an even grade of valence. Certain elements (the so-called "Artiad") are such that the compounds they generate of an odd grade of valence are more stable than the compounds of an even grade of valence. Other elements (the so-called "Perissads") are such that the compounds they generate of an even grade of valence are much more stable than those of an odd grade.

Sometimes, indeed, so far does this tendency proceed that while a whole series of representatives of compounds of an even

*) Guichard. C. R. (1899). 129. 1239—1242.

type are known, compounds of an odd type are completely wanting; and vice versa.

For example, no mono-valent, trivalent, or pentavalent compounds of carbon are known, though divalent (eg. CO) and tetravalent compounds are well known. Aluminium only produces trivalent compounds. The whole phenomenon arises out of the fact that the intensity of the force with which atoms are attracted by an atom A when in grades of valency n and $n-2$, $n-4$, $n-6$ &c. is usually (for an unknown reason) greater than the intensity of force which it attracts atoms when in the intermediate grade of valence $n-1$, $n-3$, $n-5$. So that the compounds of valency grade n produced by A pass directly to compounds of the grade $n-2$, $n-4$, $n-6$, without producing the intermediate compound of grade $n-1$, $n-3$, $n-5$ &c. in the way previously explained. It is only in the case of very few elements (for example W and Mo) that compounds of an even and compounds of an odd grade of valence are of an equal degree of stability.

A study extending over many years of the data relating to the various stabilities of the compounds of different valency grades of the different elements has long convinced me that viewed under suitable external physical conditions an element could give rise to compounds of any given grade of valence between unity and eight; and that these rarer forms of union are unknown simply on account of the experimental difficulties of preventing the unstable grades of union going over into more stable grades.

For some remarks on the change of properties exhibited by an atom when it changes its valence (a result of this change of force referred to above) I refer the reader to pp. 32—34.



Appendix B.

On the critical temperature of decomposition of chemical compounds, and its bearing on the phenomenon of life.

So far nobody seems to have considered the question whether to every chemical compound there exists a definite critical temperature and pressure of decomposition. Yet I think the following considerations show that such constants probably do exist. Suppose we place a given compound (say CaCO_3) in a closed cylinder and subject it to a continually increasing temperature, keeping the pressure constant by means of a weighted piston. Then at a certain definite temperature range the compound will begin to decompose. Suppose, now, we increase the pressure sufficiently; then the decomposition ceases, and the substance can now bear a higher temperature than before without decomposition.

Proceeding in this way, it is, I think, obvious from the finite nature of the mass of the atoms, and from the limited intensity of the forces holding them together in the molecule, that ultimately at some definite finite temperature the external forces tending to drive the atoms apart will become equal to the maximum internal forces that the atoms can exert on each other in the molecule.

It therefore follows that above a certain definite temperature, depending upon the nature of the molecule, no pressure, however great, can prevent the substance from completely decomposing. This temperature and pressure, above which a compound is incapable of existing, we will call the critical temperature and pressure of decomposition of the compound. The critical tem-

perature and pressure of decomposition would therefore be completely analogous to the critical temperature and pressure of liquefaction of a compound — only in the latter case we are dealing with the temperature whereat a certain molecular condition of existence disappears, and in the former case with the temperature whereat a certain atomic condition of existence disappears.

Since atoms are a very much more finely divided form of matter than molecules, it is clear that the critical temperature of decomposition of a compound must be a very much sharper and clear-cut constant than its critical temperature of liquefaction.

The critical temperature and pressure of even very unstable compounds is usually very high, provided there exists but a few atoms in the molecule.

For example, AuCl_3 , ozone, and the oxides of nitrogen, although very unstable at ordinary temperatures, seem capable of existing at very high temperatures. In general, the greater the number of atoms contained in the molecule, the lower the critical temperature of decomposition, as is evident from the general observation that the more complex a compound is the easier it is to decompose. Many of the very complex carbon compounds — for example, the proteids — have, on account of their complexity, critical temperatures of decomposition which lie very close to the normal temperature of the earth's surface.

If, now, by some means we proceed to add on atoms to such a molecule so as to make it more complex, we would steadily lower its critical temperature of decomposition, and by adding on a suitable kind and number of atoms we could reduce the critical temperature and pressure of the compound until they coincided with the normal temperatures and pressures which hold upon the earth's surface. Such a compound would be possessed of an extraordinary sensitiveness to external influences on account of the sharpness of the constants called above the critical temperature and pressure of the compound.

The slightest increase of temperature, or decrease of pressure would serve to throw it into a condition of rapid chemical decomposition, whereas a slight increase of pressure or decrease of temperature would cause it to cease to decompose. Even did we

maintain the external temperature and pressure exactly at the critical temperature and pressure of the compound, nevertheless the external impulses which are continuously pervading all space in the neighbourhood of the solar system, beating intermittently upon the sensitive substance, would be sufficient to throw it into a series of rapidly alternating states of decomposition and repose.

One must be struck with the large number of important changes which occur among complex carbon compounds between the small range of temperature 0° — 100° C, and it is obvious that this fact must have a deep and fundamental connection with the phenomenon of life.

I suggest, that the temperature range of animal life is probably nothing more or less than the range of the critical temperature of decomposition of a series of certain very complex carbon compounds which are grouped together under the name "protoplasm", the external pressure of the atmosphere coinciding roughly with their critical pressures of decomposition.

In fact, I suggest that just as a tuning fork is set into motion by vibrations of a certain definite frequency and by no others, so living matter is so constructed as to respond continuously to the incessant minute fluctuations in the external conditions which hold upon the earth, the state of response being what is known as life. The temperature of animal life keeps remarkably constant, as it should do on our supposition, a temperature too high exceeding the critical temperature of decomposition of living matter and so destroying its structure, while a temperature too low causes it to cease to decompose, and the living matter becomes inactive.

This conclusion is strengthened when we come to survey the nature of the complex compounds carbon generates with hydrogen, oxygen, and nitrogen — which are the elements out of which the protoplasm is principally composed. We find that they are characterised by their feeble stability, and, as a consequence of this (see chap. II p. 120—125) by their fusibility and volatility. In fact so unstable are these compounds that the whole

of organic chemistry is destroyed at a red heat. Moreover from the facts discussed in chapter II, we should expect a compound at its critical temperature and pressure of decomposition to possess certain definite physical characteristics which agree with the known properties of protoplasm. For since the atoms in its molecule attract each other but feebly, the molecules themselves would also attract each other but feebly; it would therefore be soft, probably of a fluid or semi-fluid nature; since its molecules are very complex it would not be volatile; it would possess a mobile nature, since would be in a state of incessant change.

The difference in the functioning of the different parts of the protoplasm which exhibits itself in the tendency to produce different organs, may be due to different sensitiveness of the different parts of the protoplasm to different external influences, caused by the substitution of minute quantities of heavy elements for the other elements in its structure, the substitution altering to a slight extent the critical temperature of decomposition. Such would be selenium in place of sulphur; sulphur substituted for oxygen; copper, zinc, or manganese replacing iron; phosphorus, arsenic, or even vanadium itself playing the part of nitrogen in the complex vital molecules.

In fact, just as a tuning fork when slightly weighted is set into motion by vibrations of a slightly different frequency to those which set it in motion when unweighted, so also protoplasm weighted with the presence of minute quantities of heavy elements responds to slightly different minute fluctuations in the external physical conditions upon the earth's surfaces than those which set the normal protoplasm into a state of response.

This is probably the reason why certain heavy elements (for example Arsenic) are retained in perceptible quantities in certain organs of different animals, and are almost entirely absent from other organs.

We will now proceed to discuss the question whether life can exist under other conditions of temperature and pressure than those which now exist upon the earth. To do this we must consider somewhat more closely the nature of living matter. Living protoplasm is a very complex chemical compound in a

state of continual internal change, or better, in a state of dynamical equilibrium; it is obvious that the surrounding conditions, namely, the temperature and the forces, such as gravity, to which all matter is subject, must be of such an intensity as to render possible the attainment and maintenance of this "balance" of motion in the living complexes, otherwise all life would soon cease. Of all the terrestrial elements there appears to be but one which, under the present thermal conditions, is capable of generating these ever changing complexes, in which this necessary state of dynamical equilibrium is attained. This element is carbon, and this is why, at ordinary temperatures, it forms the basis of life.

The carbon atom is tetravalent. In other words, an atom of carbon is able to control or regulate the motion of four atoms akin to the hydrogen atom, or two atoms akin to oxygen atom. If the temperature be increased, the relative motion of the attached atoms is increased, and the carbon no longer appears able to keep them together. On the other hand, if we reduce the motion of the attached atoms by lowering the temperature, we get one system of atoms continually combining with other systems of atoms, and thus the compounds grow more and more complex. Conceive now of an enormously complex body, whose molecules, if such a compound has molecules in the ordinary sense of the word, consist of system after system of atoms, all in motion, atom circulating about atom and system about system — a molecule so vast and so complex as to be in itself a kingdom. Then imagine the temperature to be very slowly increased; the motion of the intricate streams of atoms within the molecule become more and more vehement, until a point is reached where the controlling force is just unable to keep captive the whirling systems, but yet sufficient to maintain and direct an harmonious system of atomic movement within the molecule. Consequently the molecule is continually breaking down. As fast as it breaks down, materials continually stream into the sphere of this molecular motion, circulate in its system, and stream out again. Thus the molecule is constantly replenished. Hence its molecular existence is a continual metathesis, and as in a vortex ring, the motion when once

created goes on for all eternity — if only the stream of replenishing atoms be maintained and the temperature properly adjusted. It is from such state of harmonious motion as that here pictured, and made possible by the presence of jarring atoms of nitrogen, which by their changeable attractive capacity render the system so unstable, that in all probability the phenomenon of life arises. Before life can arise we must probably have (1) an atom, like carbon, which is capable of linking together a large number of atoms; (2) a great constancy in the attractive capacity of the central linking atoms, in order that the gliding away of the various systems may be attained as soon as the proper amount of motion, and consequent pull, is reached; (3) a motion of such an intensity among the atoms as just to overcome the attractive power of the controlling carbon atoms, or system of atoms.

This constant intensity of motion implies a constancy of temperature; it will be noticed that the temperature of men and mammals generally keeps remarkably constant, and the external conditions are such as to allow this constant temperature to be maintained. Indeed, life in its present form can only flourish between very narrow limits of temperature. It is within these limits only that such complex and unstable carbon compounds can exist in a state of continual decomposition — a state which is essential to the maintenance of life. Above this temperature these compounds break down into more stable forms of matter. Below this temperature the continual metathesis ceases. This necessary temperature being, in a sense a measure of the attractive power of the central element, it is obvious that it will depend both upon the nature of the central linking element, in our case carbon, and upon, but to an unknown extent, the external forces, such as gravity, to which matter is subject.

Conceive now the temperature of the earth and all objects thereon lowered by say 250°C . How would the carbon compounds appear to the eye of man? They would be hard, and in many cases transparent or translucent solids; in other cases, opaque. They would in fact bear a remarkable resemblance to the silicates — vastly complex bodies having exceedingly high molecular weights. At such a temperature, we should probably

be entirely ignorant of the inner structure of the carbon compounds. We might, indeed, notice that when (say) acetyl chloride and many organic compounds are heated up to what would appear a red heat, the organic compound is attacked. Such reactions, however, would possess no more significance to the chemist living at that low temperature, than the fact that lead oxide attacks siliceous matter at high temperatures has for us. It will be seen, therefore, that in complexity the silicates can well be compared with the most complex organic bodies, and have probably internal constitutions quite as intricate as those exhibited by the most abstruse carbon compounds. The fundamental difference between the two sets of compounds is essentially one of temperature, — the carbon compounds being at ordinary temperatures much nearer their melting and decomposing points than the silicates. This property carbon has of acting the rôle of the fundamental element in the animal organism is then, probably, a mere function of the temperature, and greatly dependent upon the unstability of its compounds at this temperature.

We are therefore justified in asking whether there is any other element which at some other temperature could play the part now played by carbon at ordinary temperatures in living organic matter?

Silicon is such an element.

Silicon, like carbon, possesses a high and constant valency. There is indeed a great similarity between the compounds of carbon and silicon. The number of complex double oxides of silicon is innumerable. True, we cannot effect the synthesis of the compounds and determine their constitution as in the case of the complex carbon compounds; but in great measure this is an accident of temperature rather than anything else. If we could work at a temperature of 700—1000° C as easily as at ordinary temperatures, there is little doubt that a great flood of light would soon illuminate this portion of our science. We might indeed shortly be able to generate a "Chemistry of the Silicon Compounds".

There probably exists for silicon, as well as for carbon, a transitional or critical temperature range whereat a large number

of unstable silicon compounds are capable of momentary existence, a higher temperature rendering their existence impossible, while a lower temperature would make the compound stable.

At this transitional temperature the complex compounds would be capable of a continual metathesis, and thus give rise to the phenomenon of life; only in this case all forms of life would have as the determining element not carbon, but silicon.

Seeing that in the case of carbon this temperature occurs when many of its compounds are in a semi-fluid condition, and near their decomposing point, we should expect the corresponding temperature for silicon compounds to occur when they, too, are in a pasty or semifluid condition.

Now we know that the temperature and pressure on the world's surface has not always remained exactly the same as at present. In the earliest times the world's surface was a white hot sea of molten rock surrounded by vast masses of vapour, and its temperature only gradually cooled down to that which at present holds. Consequently the structure of living matter (if it existed at all) must have altered the more the further we go back. For at ordinary temperatures and pressures living matter contains the exact quantities of the necessary elements (namely carbon, hydrogen, nitrogen, oxygen, sulphur and phosphorus) to make its critical temperature of decomposition coincide roughly with the conditions which hold upon the earth at the present time; as the temperature and pressure of the world's surface altered, the relative quantities of these elements contained in living matter would also have to alter in order to make its critical temperature and pressure coincide roughly with the new temperatures and pressures. In general, the higher the temperature and pressure, the more pronounced would be the tendency to let heavier and less volatile elements enter into its structure; and at the highest temperatures living matter must have been composed out of altogether different elements to those which at the present time compose it. I suggest that the structure of living matter has, like most other things, for example, the atmosphere, undergone a continuous process of evolution (and is still undergoing it) with the changing external conditions; and that at the time when the earth was a white hot

fluid sea, life still existed in a form quite different to that which now exists, the chief elements entering into its structure being at that time heavy elements; and that as the world gradually cooled, the heavier elements were gradually eliminated and the lighter elements took their place, by a natural process of circulation such is even at the present day going on, until finally the composition of living matter assumed its present one.

Have we any evidence which supports the view that living matter did not start originally with carbon, hydrogen, oxygen, and nitrogen as its fundamental elements, but started with elements of far higher atomic weights, such as silicon, phosphorous, sulphur, of which only vestiges now remain in the protoplasm? It must be remembered that our evidence could only be indirect; such life could have thrived to an enormous extent in the white hot molten siliceous matter which covered the earth's surface in bygone ages, and yet have left no traces of its existence behind; for when such forms of life died, their bodies would but blend again into the molten rock, in the same way that a jelly-fish dies and blends into the ocean of salt water, without leaving a vestige behind to show that it has been and gone; except under exceptional circumstances, organised matter when once dead, very quickly disintegrates. However many remarkable siliceous minerals exist — for example "Asbestos" or "Mountain leather", whose peculiar fibre-like structure may perhaps be due to its previous organic nature ages and ages ago. Again, among some of the most rudimentary forms of organised existence, for example the diatoms and sponges, silica still remains in considerable quantities.

Now it is clear that in consequence of the progressive cooling of the earth, the range of temperature whereat silicon possesses the capacity for forming the central element of living matter would be soon passed and hence its complexes would solidify out into stable masses, thus causing all life to cease.

But if carbon entered more and more fully into the composition of living matter, and the silicon as steadily solidified out as the cooling continued, the critical temperature of decomposition (or temperature whereat life is possible) would become progressively lower in proportion as the amount of carbon in the organism

increased, and hence the cooling of the surrounding medium, and the alteration in the living temperature of the organism would proceed together and keep pace — the temperature of the organism lagging slightly behind the falling temperature of the surrounding medium (as it actually does now in world life) just as the temperature of a thermometer placed in a cooling liquid, lags slightly behind that of the liquid in which it is placed.

The silicon age would thus blend imperceptibly into the carbon age, and when the modern thermal conditions were attained, the carbon would have long since completely replaced the silicon in living matter and the last era of organic existence would have begun. It will be noticed that some of the most rudimentary forms of life with which we are acquainted with, namely, some of the diatoms and sponges, still posse the power of secreting silica in large quantities.

Let me now quote some other facts in support of our suggestion that as the thermal conditions of the earth altered, there was a corresponding alteration in the composition of living matter, the denser and less volatile elements, steadily solidifying out and their places being filled by analogous lighter and more volatile elements.

Albumen contains a small quantity of loosely bound sulphur which does not appear to be a very intimate constituent of it; no one knows the function of this sulphur; according to my theory, it is simply lingering on, the relics of a time when it almost entirely replaced oxygen in the organism. With the falling temperature of living matter, sulphur was superceded by the lighter and more volatile oxygen and consequently the sulphur that remains is merely an inert mass, separating out on account of its heaviness in exactly the same way I have supposed silicon to have separated out in previous ages.

Much the same applies to the phosphorus in the tissues of the brain and nerves. It has been almost entirely replaced by the lighter and more mobile nitrogen. The small amount of phosphorus present remains mainly because it can perform functions which nitrogen cannot. Traces of a still heavier member of the same group of elements, namely arsenic, have been recently

found in certain animals, where it partially replaces the phosphorus in nucleinic matter*). In these cases we have a whole chain of chemically analogous elements replacing each other in continually decreasing amounts as they increase in heaviness, thus:

{	nitrogen	(at. wgt. 14)	abundant in protoplasm
{	phosphorus	(at. wgt. 31)	less abundant in protoplasm
{	arsenic	(at. wgt. 75)	minute traces
{	oxygen	(at. wgt. 16)	abundant
{	sulphur	(at. wgt. 32)	less abundant
{	selenium	(at. wgt. 79)	minute traces, if at all
{	carbon	(at. wgt. 12)	abundant
{	silicon	(at. wgt. 28)	traces

It is very probable that formerly abundant elements in living matter have long since ceased to perform any vital function and solely remain as witnesses to the process of evolution, much as the gills on the neck of the embryonic babe remain to bear witness to the aqueous origin of its ancestors.

In the current textbooks of Physiology but little is said concerning the presence of mineral matter in protoplasm; the subject is usually treated as of an obscure and unimportant nature. But who can say whether further studies on the minute quantities of "ash" found in all living matter, and on the general secretion of mineral matter by living beings, may not ultimately lead to the discovery that the mobile protoplasm of today evolved in a continuous manner from the molten minerals of the past?

The range of life would then widen magnificently out from the few million years of Lord Kelvin, to countless billions of years when the world was a white hot globe and its surface a sea of rolling fire. From first principles, indeed, it is very improbable that life could exist only within such narrow limits of temperature and pressure such as are at present prevalent upon the earth. Out of the almost infinite time which has passed before the world cooled to its present state, and the ages

*) Gautier. Chem. News. March 23rd. 1900.

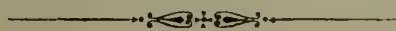
that still must run ere the world reaches the absolute zero of temperature, is it to be imagined that during an only infinitesimal portion of this time could organised life exist?

To assume that this is the case is to place oneself in the position of those early astronomers who held that the sun and stars and the infinite universe itself revolved about our puny earth as centre. Again, are we to assume that out of an unknown but probably enormous number of elements, only some four elements, hydrogen, oxygen, nitrogen, are capable of producing vital matter?

When we study the properties of these four elements and compare them with those of the other known elements (see the affinity plates at the end of the book) we find that there is nothing which inherently distinguishes them from the other elements; every property possessed by them is shared to a greater or less extent by the other elements also. Why, then should we imagine that only these four elements can give rise to living matter? Why they enter so largely as they do into the composition of living matter is probably a pure accident of temperature and pressure; they merely happen to possess atoms of the proper degree of lightness and attractive power corresponding to the conditions of temperature and pressure holding upon the earth, which makes them more adapted than the other elements to enter into the constitution of living matter. There exist, however, in space numberless vast planets and dark suns and white hot fluid globes whose physical conditions differ utterly from those which hold sway upon the earth. It is incredible to suppose that they are entirely void of life. No! on such mighty globes forms of life must also exist, life on a far grander scale of creation than any that has existed or ever will exist on our puny earth, life composed out of entirely different elements to those which compose our wordly living matter. We have suggested in chapter VII, that by altering the external conditions under which we view an element, we can make it assume in succession the successive different chemical conditions which the various elements are in at ordinary temperatures and pressures.

If this is so, it is difficult to avoid the inference that under other external conditions other elements would enter into the structure of living matter. Life is old, old as the universe itself. It has always existed generally disseminated throughout the universe, and always will exist no matter what happens to our little earth. The protoplasm of the earth is but the product of evolution of untold aeons of ages, coming down to us in an unbroken line from times when the world was a white hot fluid mass; all the elements have circulated successively through its structure and then passed out again; first at the highest temperatures came the heaviest and least volatile elements, then as the temperature fell they gradually solidified out and their places were filled by analogous lighter and more volatile elements, until at last living matter assumed its present composition. But this replacement of denser by lighter elements is now almost complete, for the principal elements already present in living matter are carbon, nitrogen, oxygen, and hydrogen; and these, it will be noticed, are the very lightest non-metallic elements.

No lighter elements, then, can replace those already present in the organism, and therefore there can be no further very great alterations in the temperature of living matter in the coming ages; but the world is still cooling; consequently age by age, century by century, the contrast between the temperature of living organic matter and the temperature of the surrounding medium is becoming more and more accentuated, and the difficulty of maintaining life is steadily increasing. So that so far as this world is concerned, organic life has probably entered into its last stage of evolution.



Appendix C.

On the possible significance of alcohol drinking.

When a child I live in a small town in South Wales. In the town the people spoke only English; in the remoter country districts the peasants still spoke Welsh.

The language that these peasants spoke had for me at that time no interest or significance.

It was a rude, imperfect dialect which was only spoken by uneducated people.

To me now, in after years, how different appears that rude peasant dialect! It signifies for me now the relics of a by-gone time when this poor dialect was a great world speech — such as English is now — and these rude peasants the representatives of a mighty people — the Kelts — whose armies swept in waves of living valour from out of Asia into lands so distant as Ireland, Spain, and Asia-minor.

Now what has worked the difference in my mental attitude? Solely increase of knowledge. When a child I knew nothing of the Kelts nor of their history. And so it is generally. A treatise on Bessel functions has no earthy interest for a Matabele warrior; the mathematical physicist is deeply interested in such a book; the interest of the mathematician is the result of a knowledge of the use and possibilities of such functions. The uninterest of the Matabele is due to his ignorance.

Many matters appear to possess no interest or importance to us simply because of our ignorance. Suitably viewed such facts become pregnant with world-wide consequences; for example, the blind hates and bitternesses which exists between peoples of different races has possibly no particular significance for the

average man, except perhaps as a deplorable fact. To a scientist these racial hates inspire the greatest interest, for in his eyes they are but the outward play of those mysterious organic forces which cause evolution and the differentiation of species.

The almost universal drinking of alcohol, and the vice of drunkenness, which exists among all peoples and in all times of which we have any record, is another phenomenon of the same kind.

We propose here to review this last matter as a scientific problem, and gravely consider the physiological reason why men of all animals have this natural instinct after strong drinks most strongly developed.

Is it the manifestation of some great and imperfectly understood organic tendency, or is it only of the nature of a disease?

We proceed to discuss this question solely from a chemical stand-point.

One condition which seems indispensable for the manifestation of vital activity is fluidity. All living matter is bathed in fluids and it itself has a mobile semifluid constitution; all facts point to the conclusion that the condition of fluidity is intimately connected with life; it is even said that life first originated in the fluid sea and thence spread to land.

Certainly the observation that by far the greatest part of living matter consists of water, either free or combined, lends strength to this supposition.

The reason of this mobile and semifluid condition of living matter becomes manifest when we begin to study its chemical nature. Living matter is a complex system of atoms in eternal breakdown. The very condition of life seems change. Only in a semifluid condition can take place that continual redistribution of matter which, while preserving the form of living matter intact, supplies that flux of atoms which counterbalances its continuous decomposition.

Were the external physical conditions as regards temperature and pressure such as to render the existence of matter in a fluid or semifluid condition impossible, then life as we know it would be incapable of existing. For example, at very low temperatures,

all matter solidifies and the fluid condition as a phase becomes impossible. Even the most volatile gases first condense to liquids and then change to solids, so that at a temperature approaching the absolute zero we look out upon a frozen solid world.

The constitution of living matter must therefore be so adjusted to the external physical conditions as regards temperature and pressure that it continually maintains this condition of fluidity. When we contemplate the history of the world we find that these conditions have in former times been widely different from those which at present hold. There was a time when the world was a white-hot sea, when the moon had not yet been flung off by some mighty catastrophe from the revolving glowing mass. As ages passed the world cooled and cooled, until finally the temperature conditions which now reign were attained.

But the process of cooling is not finished; the world is still cooling and there will surely come a time when the average temperature of the world will sink from its present value (15°C) to 0°C , to -10°C , -100°C , and finally below the freezing point of hydrogen itself.

Even at the present time the temperature of the world is only slightly above that temperature at which all the water on the earth will pass into the solid condition. Indeed the process of solidification has already commenced. Vast regions are found where the water has already permanently passed into the solid condition; and the regions will extend with time until the seas and the mighty oceans themselves will freeze and be converted from top to bottom to a vast mass of ice.

Water will appear to the inhabitants of future days as solid deposits of mineral matter, presenting to them much the same appearance as the white masses of marble rocks in certain parts of the world appear to us.

At first sight it would appear that the effect of this universal solidification of water will have upon the life of the earth in the form we know it, will be its absolute destruction. For with the passage of water into a solid state the existence of living matter in a fluid or semifluid condition becomes impossible.

Water is one of the most volatile and important constituents of living matter; all the tissues are bathed in watery fluids, and by far the greatest portion of living matter is actually composed out of water. Upon the fluidity of water hangs the mobility and fluidity of living matter as we know it.

It is true that the freezing point of water may be lowered even to a considerable extent by the addition of impurities to it. For example, a mixture of water and salt can remain fluid at temperatures very much lower than that at which pure water freezes. Yet even this artificial lowering of the freezing point of water will only enable us to stave off for a time its universal solidification in the tissues and the consequent passage of living matter into a solid frozen condition.

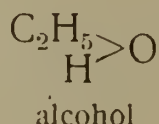
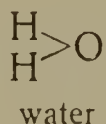
Were living matter a rigid unadaptable machine, one might well look with despair upon the prospects of life in the coming ages of cold and eternal night. Many facts we know, however, point to the conclusion that living matter possesses the power of adapting itself to changing external conditions; for example, it is a well known observation that by gradually rising the temperature of water in which certain organisms live, we can in the course of time cause them to live and flourish in water so hot that specimens of the same organism which had not become acclimatised to the changed temperature, are at once killed when placed therein. The question is, therefore, in what direction can living matter change its constitution in order to adapt itself to temperatures much below that at which water enters into a solid condition?

One thing appears certain. If living matter is to avoid being frozen hard with the falling temperature, the water as such must be gradually eliminated from the organism and its place taken by another liquid which remains fluid and mobile under conditions which render the existence of water as a fluid impossible.

Now is there any other fluid which perhaps could take the place of water in living matter and fulfil this condition? Alcohol seems to be such a fluid; alcohol freezes at -130°C , water at 0°C .

Moreover, of all the known compounds alcohol is the one which approaches both chemically and physically nearest to water in properties.

Both are mobile fluids; both are great solvents; both have a very similar constitution — alcohol, in fact, is water in which a hydrogen atom is replaced by the heavier radicle C_2H_5 , thus:



Alcohol can perform many of the functions of water; for example, just as water can combine with molecules to form "Water of Crystallisation", so also alcohol can, and we can likewise speak of "Alcohol of Crystallisation".

Moreover alcohol is, like water, though to an enormously smaller extent, associated with living matter.

It is the product of fermentation in enormous quantity by the lower forms of life, and occurs to a greater or less extent in fermented ripe plants and fruits.

It is therefore by no means inconceivable that alcohol could enter into the constitution of living matter to an enormously greater extent than it does at present, and thus replace the water as the fluid which bathes the tissues.

Moreover there even seems to be at hand the mechanism by which such a replacement could be brought about; certain of the lower forms of life can manufacture alcohol as a product of their vital activity.

The whole phenomenon of alcoholic fermentation is an instance of this fabrication.

We have only to conceive that this fabrication of alcohol takes place to an increasing extent in the living body itself. These alcoholic ferments can be conceived to enter as the temperature falls to an increasing extent into the constitution of living matter, and thus to gradually increase the store of alcohol in the body itself. So that when the temperature falls below that at which water freezes, the watery fluids in the lower forms of life will have been replaced by fluids in which alcohol largely

predominates, and which, therefore, remain fluid and mobile at a temperature whereat the plant would be frozen hard if it contained only water.

The age of water life would thus gradually pass into the age of alcohol life; and the cause of the variation would be the necessity for the organism to adapt itself to the altering external physical conditions by eliminating a less volatile for a more volatile fluid.

It is in the light of this conception that we approach the treatment of the question of alcohol drinking by the human race. It is well known that men in cold climates drink alcohol in a more concentrated form than the men of warmer lands.

Coldness, in fact, seems instinctively to drive men to alcohol. And if the temperature of the world is gradually reduced, so as to replace a temperate climate by a colder one, doubtless this tendency would be greatly intensified.

I can easily imagine a process by which man first began by drinking only water — as the lower animals do now; then by drinking water with a little alcohol in it, as man does now; then as the world grew colder and colder age by age, the amount of alcohol in the drink gradually increased until ages hence man will have evolved into a creature which will drink only alcohol. Together with the increase in the alcohol in the fluids man consumed, the quantity of alcohol in the fluids of the body increased, and the quantity of water diminished, until ultimately in the course of ages the constituents of the fluids of the tissues so altered that the water was entirely replaced by alcohol. The process of evolution would then be complete; a less volatile fluid would be replaced by a more volatile one, by a process probably of the same nature that caused the less volatile elements such as sulphur, phosphorus and silicon, to be replaced by the more volatile ones such as oxygen, nitrogen, carbon and hydrogen.

Water would then exist in mere traces in the body, much as S does now, as the relics of a by-gone time when it assumed a far greater importance in living matter than it does at the present time.

Is not this tendency men have to abstain from drinking pure water and to drink instead alcoholic beverages nothing else than the beginning of the gradual replacement of the water in the human body by alcohol?

Viewed in this light the phenomenon of alcoholism assumes the greatest interest and importance, as the possible manifestation of a mighty organic change sweeply slowly but irresistibly over the whole of living matter.

It may be, however, that some other fluid — for example an oily liquid such as is found in great quantities in the bodies of fishes which live in cold seas — and not alcohol, would be the liquid which will ultimately replace water in living matter. Whether this be so or not, one thing, I think, is almost certain, and that is that if life is to continue at much lower temperatures than those which hold normally upon the earth, the water must be eliminated and its place taken by another liquid harder to freeze.



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Errata.

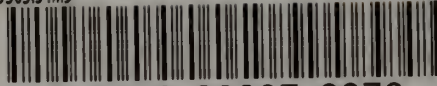
- p. 15 line 15 from bottom: *for* "solnbility" *read* "solubility".
- p. 21 line 13: *for* "für" *read* "for".
- p. 24 line 6 from bottom: *for* "constans" *read* "constants".
- p. 27 line 6 from bottom: *read* "producible by an element".
- p. 29 line 2 from bottom: *read* "corresponding".
- p. 53 line 6 from bottom: *read* "cadmium".
- p. 60 line 14: *read* "similarly".
line 20: *read* "possesses".
- p. 61 line 10 from bottom: *for* "MO₃" *read* "MoO₃".
- p. 63 line 3 from bottom: *read* "sufficient".
line 10 from bottom: *read* "Fe(SO₄)".
- p. 65 line 16 from bottom: *read* "preceeding".
line 1 from bottom: *read* "properties".
- p. 66 line 12 from bottom: *read* "building".
line 1 from bottom: *insert* "bracket" *after* "attraction".
foot-note: *read* "Schorlemmer".
- p. 67 line 3 from bottom: *after* "remarkable" *insert a comma*.
last line: *read* "Sb.Et₄.OH".
- p. 68 line 3 from top: *read* "conclusions".
- p. 72 line 3 from bottom: *read* "that".
- p. 82 line 6 from bottom: *for* "much less" *read* "much more".
- p. 85 line 3 from bottom: "Volatility" *should commence with a small "v"*.
- p. 100 line 6 from top: *for* "Ca" *read* "Ba".
- p. 113 line 14 from boitem: *read* "volatile".
line 3 from bottom: *read* "heavier".
- p. 115 line 7 from bottom: *read* "W₂S₄Cl₈".
- p. 116 line 3 from top: *read* "fluoride".
- p. 119 line 7 from bottom: *read* "molecular weight".
- p. 123 line 2 from bottom: *read* "represent".
- p. 129 line 14 from top: *read* "themselves".
- p. 136 line 21: *for* "sufficent" *read* "sufficient".
- p. 137 line 13: *for* "insufficent" *read* "insufficient".
- p. 142 line 9 from bottom: *for* "Ca" *read* "Na".
- p. 147 line 7 from top: *for* "F" *read* "Na".

- p. 157 line 10 from top: *for* "N" *read* "Na".
line 12 from bottom: *read* "large" *not* "very great".
line 9 from bottom: *read* "increases".
- p. 180 line 15 from bottom: *for* "flourine" *read* "fluorine".
- p. 189 line 15 from bottom: *for* "other kinds" *read* "some kinds".
- p. 195 line 14 from top: *instead of* " f_1, f_2, f_3 . Increases" *read* " f_1, f_2, f_3 , increases".
- p. 201 line 3 from bottom: *for* " CH_3 " *read* " NH_3 ".
- p. 204 line 5 from bottom: *for* "of ordinary temperature" *read* "at ordinary temperatures".
- p. 228 line 6 from bottom: *instead of* "special" *read* "spacial".
- p. 230 line 9 from bottom: *read* "external".
- p. 234 line 1 from top: *read* "subsequent".
line 14 from top: *read* "ordinary".
- p. 242 line 9 from top: *for* "(T', Cl)" *read* "(I', Cl)".
footnote: *for* "Jv." *read* "Jr".
- p. 243 line 1 from top: *read* "influence".
line 8 from bottom: *read* "Artiads".
- p. 244 line 7 from bottom: *read* "grade".
- p. 246 line 11 from top: *read* "pressure of decomposition".
- p. 264 line 2 from bottom: *read* "taken".



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